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XCV. *The Metallic State.*
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Introduction.

THE various theories of the metallic state have previously considered chiefly the thermal and electrical properties, since it is in connexion with these that the metals show their chief characteristics. The object of the present paper is to discuss the applications of these theories to some of the other properties of metals in the solid state, and the electrical properties will only be referred to incidentally.

SECTION I.

IN the first place it may be well to summarize critically the principal theories of the metallic state, since the descriptions of these are widely scattered throughout the

* Communicated by Prof. F. A. Lindemann, F.R.S.

literature, and are not easily accessible. The theories may be conveniently grouped under the following headings:—

1. *The Free Electron or Electron Gas Theory**, according to which the characteristics of metals are due to the presence of free electrons in the space between the atoms. These electrons are supposed to behave like a perfect gas, and on this assumption most of the electrical phenomena may be explained with fair accuracy. In particular, if the law of equipartition of energy be assumed, the theory leads to a correct value for the Wiedemann-Franz ratio. The objection to the theory is that the thermal and electrical properties indicate quite different numbers of free electrons, and that the supra-conductivity at very low temperatures is not accounted for. On these and other grounds the theory has been effectively criticized by Lindemann†. It is, however, still accepted in many quarters.

2. *The Di-Pole Theory of Thomson*‡.—On this theory the atoms of some substances, including metals, contain electrical doublets, or pairs of equal and opposite electrical charges at a small distance apart. From this point of view the part played by the electric force is to polarize the metal, or to form chains of the di-poles. When once these chains are formed, the electrons are passed along by the forces exerted by the doublets, and the electrons which move are not those in the doublets themselves. The arrangement of the doublets is upset by the thermal agitations, and on this assumption the theory gives a general explanation of the electrical phenomena including the supra-conductivity at low temperatures which was not explained by the older electron gas theory. The large amount of polarization required is, however, contrary to what we should expect if we accept modern atomic theory, and is also contrary to the values obtained by Born for the degree of polarization of ions. On these and on other grounds the theory is no longer generally accepted.

3. *The Theory of Wien and Gruneisen*§.—This theory

* Drude, *Ann. d. Phys.* i. p. 566, iii. p. 369 (1900). The subsequent literature is very extensive.

† *Phil. Mag.* xxix. p. 125 (1915).

‡ 'The Corpuscular Theory of Matter,' p. 86 and *Phil. Mag.* xxx. p. 192 (1915).

§ See Gruneisen, *Verh. d. Deut. Phys. Ges.* xv. p. 186 (1913); also Beckman, *Phys. Zeit.* xvi. p. 59 (1915).

is based partly on the theoretical work of Wien *, and partly on the empirical discovery that the ratio of the specific resistance to the absolute temperature increases at low temperatures in exact proportion to the atomic heat †. The fundamental assumptions are that the electrons are still moving freely between the atoms, but that the lengths of their free paths are determined solely by the amplitude of the atomic vibrations. From quantum considerations Wien assumes that the length of the free path is inversely proportional to the square of the amplitude of the atomic vibrations. The electron velocity is regarded as independent of the temperature, and remaining unchanged even at the absolute zero. As extended by Gruneisen the theory was the first to give any quantitative explanation of the decrease in electrical resistance under pressure, which was accounted for on the assumption that the increased pressure increased the frequency, and hence diminished the amplitude of the atomic vibrations, and that this effect more than outweighed the reduction in distance between the atomic centres. Quantitatively the theory gave a pressure coefficient of resistance of the right sign for all the normal metals ‡, and almost exact agreement for copper, silver, gold, and aluminium, but not such good agreement for the other metals, especially those of low melting-points. The theoretical treatment is, however, open to criticism in that it draws on both of the fundamentally-opposed theories of Wien and the electron gas theory §, and also that the fundamental treatment of Wien assumes the energy quanta to be located in the individual atoms instead of in elastic waves.

4. *The Electron Lattice Theory of Lindemann* ||.—This theory rejects the whole conception of electrons moving freely as in a gas, and considers them as behaving like a perfect solid and being situated on a space lattice interpenetrating that of the atoms. It is assumed that though attracted according to the inverse square law by the ions at distances greater than the atom's radius, the electrons are repelled at distances less than a certain value r_0 , and hence that at some critical distance the attractive and repulsive forces balance and the electron is free to move. The theory does not predict the Wiedemann-Franz ratio,

* *Sitzber. d. Berlin. Akad.* p. 184 (1913).

† *Ibid.* p. 306 (1911).

‡ Bismuth is abnormal.

§ See Bridgman, *Proc. Am. Acad.* lii. p. 640 (1917).

|| *Phil. Mag.* xxix. p. 126 (1915).

but does not contradict it. The great advantage of the theory is that the electrical and thermal properties are no longer in conflict, since an electron lattice can be shown to behave as an ionic lattice would do at a very low temperature, and in this way a high heat conductivity is accounted for without attributing any measurable heat capacity to the electrons. The theory has been criticized on the grounds of improbability on the one hand, and of instability of the resulting structure on the other.

5. *The Theory of Bridgman* *.—The idea of this theory was to retain as much as possible of the electron gas theory, and yet avoid the discrepancies between the thermal and electrical requirements. It is assumed that the electrons pass freely *through* the atoms, with velocities given by the equipartition value as in the older theory, the resistance being caused by the difficulty of passing from one atom to another. The electrons carrying the current are small in number compared with the atoms, but constant in number, and at low temperatures, when the atoms are in "contact," the electrons pass freely from one atom to the other. But at higher temperatures gaps appear between the atoms, and these gaps cause the resistance in the same way that the collisions caused the resistance in the older theories. The bulk of the dynamical arguments of the older theory can be applied to the Bridgman theory, substituting "gaps" for "collisions"; but a much longer free path is possible, since the gaps do not necessarily appear between every two atoms, for there may be several atoms in a long string before the gap is met with, and in this way the thermal and electrical requirements are reconciled. Bridgman's results for the effect of pressure on the Wiedemann-Franz ratio were not in agreement with his earlier view of thermal conductivity as due entirely to electrons, and he later regarded a considerable portion of the conductivity as due to the atoms, the energy being passed in a series of waves from atom to atom, much as an impulse will travel down a row of billiard balls in contact. In this respect the theory is fundamentally opposed to that of Lindemann, in which the thermal conductivity of the atomic lattice is considered negligible at ordinary temperatures. Bridgman, in fact, criticizes the Lindemann view on the grounds that, whilst the electron lattice by itself will have a high thermal conductivity if the Debye

* Phys. Rev. ix. p. 269 (1917); xvii. p. 161 (1921); xix. p. 115 (1922).

elastic wave theory be accepted, the same conclusion is not justified when the electron lattice is interpenetrated by that of the atoms. On the whole the balance of evidence favours the Lindemann view, since it seems probable that the atomic and electron lattices with widely differing frequencies would not interfere with one another; whilst if the Bridgman theory is accepted, it is strange that salts should have such a low conductivity when their constituent ions are closer than the atoms in a metal. It is also by no means clear why the heat conductivity of metals is almost independent of temperature if the Bridgman view is adopted. The later developments of the Bridgman theory are more complex, and he now regards the electrons as passing between the atoms in some metals, and through the atoms in others. The theory undoubtedly suffers from drawing on rather fundamentally opposed conceptions; for, as pointed out by Bridgman, a motion through the atom with no resistance is only likely to occur in some kind of a quantized orbit, and it is hardly likely that the resulting velocity would vary according to the older equipartition value; whilst the assumption that the electrons are few in number compared with the atoms, and yet constant in number, is most improbable. If the free electrons are not equal in number to, or some simple multiple of, the numbers of atoms, we should expect their number to be a variable given by an equation of the type $n = n_0 e^{-Q/RT}$, which would give a wrong temperature coefficient.

The above theories are all more or less in agreement with the electrical properties of the metals, and it is doubtful whether a consideration of these properties alone will enable a final selection to be made.

SECTION II.

The first of the other properties which it is desired to consider here is the compressibility, and in order to make the argument clear, it is again necessary to refer to the previous work.

The modern theory of compressibility is due chiefly to Born*, and was developed originally for simple ionized salts such as the alkali halides, in which the ions in the crystal are regarded as bound together by electrostatic attractions varying inversely as the square of their distance

* *Ann. d. Physik*, lxi. p. 87 (1920).

apart. The oppositely-charged ions are thus drawn together until the attraction is balanced by a non-electrostatic repulsion, due presumably to the fields of force produced by the electrons revolving in their orbits. The fundamental argument used by Born is to represent the potential energy of a unit cube by an expression of the type $\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n}$,

where the first term refers to the electrostatic attraction and the second to the non-electrostatic repulsion, which is assumed to vary as an inverse power of the distance*.

In this equation the first term is definitely established, the inverse square law for the electrostatic attraction having been proved experimentally by Born from measurements of dielectric capacity and refractive index for long wavelengths, and by Slater † from accurate compressibility data. The factor a can then be calculated for a series of point charges if the lattice type is known.

The second term is, however, much less satisfactory. Qualitatively with large values of n it gives a repulsion increasing very rapidly at small distances, in agreement with what is required, but it has little real justification. From measurements of compressibility it was found by Born that $n=9$ (approximately) for most of the alkali halides, except for the lithium salts for which $n=5$. For calcium fluoride $n=7.5$, whilst for magnesium oxide $n=4.1$, according to data given by Hund ‡. According to the very accurate work of Slater, the simple Born theory of a repulsion according to an equation of the type $\frac{b}{\delta^n}$ is definitely not in agreement with the facts, and

there is indeed little reason that it should be. From the figures given above it can be seen that with the typical alkali halide, sodium fluoride, the value of n is about 9, whilst for magnesium oxide, which has the same crystal structure, the value of n is only about 4. Now, if our views on atomic structure are correct, Na^+ and Mg^{++} ions, whilst differing in dimensions, are identical in electronic structure, and differ only in the nuclear charges, which are 11 and 12 respectively. Similarly, the F' and O'' ions are identical except for the unit difference in nuclear charge. Since

* In the more elaborate extensions of the theory an additional term is introduced to allow for the polarization of the ions in each other's fields, but this is omitted here for simplicity.

† Phys. Rev. xxiii. p. 488 (1924).

‡ Z. Physik, xxxiv. p. 833 (1925).

$n=9$ approximately for all alkali halides, it is unlikely that a difference of one unit in the nuclear charge would cause such a profound alteration in the value of n for sodium chloride and magnesium oxide, and it would seem much more probable that n is really a complex function of the distance, and that the great difference between the values of n in the two cases is due to the fact that ions are pulled much closer together in magnesium oxide, owing to the increased electrostatic forces, which at constant distance are as 4:1 in magnesium oxide and sodium chloride respectively.

In attempting to apply the above theory to the compressibility of metals, the electron lattice theory is clearly the most attractive, the obvious suggestion being to consider the electrons as taking the place of the negative ions. This point of view has been adopted by Bridgman, especially for the face-centred cubic calcium, which he regards as having the calcium fluoride type of structure with electrons replacing the negative fluorine ions. The compressibility results may be summarized as follows:—

(1) The absolute compressibilities of the alkali and alkaline earth metals are much greater than those of their salts; *e.g.*,

Potassium chloride $K = 4.0 \times 10^{-6}$.

Potassium metal $K = 35 \times 10^{-6}$.

For other metals the compressibilities are greater than those found for salts, except for some metals of high melting-point for which measurements with the corresponding salts have not yet been made.

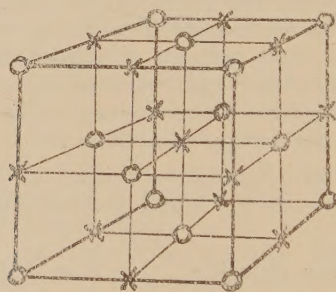
(2) The application of the simple Born Theory leads to a value of the right dimensions for the compressibility, but any attempt to use a Born term $\frac{b}{\delta^n}$ for the energy due to the non-electrostatic repulsion leads to values of n much smaller than those deduced and confirmed by Born for the corresponding ions in salts.

We thus appear to have reached a point at which the electron lattice theory, whilst satisfactory from some points of view, seems to fail when applied in detail. It is the object of the remaining sections of this paper to show that this apparent failure is due to the omission of some important factors, and that, when properly applied, the electron lattice theory is able to give a picture of the metallic state which is in general agreement with the observed facts.

SECTION III.

The first and most obvious objection to the above application of the electron lattice theory to the compressibility, is that it appears incompatible with the electrical conductivity. Thus if we take a univalent face-centred cubic metal as having the sodium chloride type of lattice shown in fig. 1, the Born theory considers the positive and negative ions as attracting one another until the electrostatic attraction is balanced by the non-electrostatic repulsive force. For convenience such ions will be referred to as "in contact"; but this is not to be taken as implying the existence of any sharp bounding surface. If, therefore, the attraction and

Fig. 1.—The Sodium Chloride Structure.



O +VE OR Na^+ IONS.

X -VE OR Cl^- IONS.

If a univalent face-centred cubic metal has this structure, the positive metallic ions are shown as circles, O, and the negative electrons as crosses, X.

If a univalent face-centred cubic metal has this structure, the positive metallic ions are shown as circles, O, and the negative electrons as crosses, X. repulsion are balanced when the electrons are in the positions shown in fig. 1, it is clear that they cannot move through the metal without passing very much closer to the atoms, when repulsion would occur; a similar objection arises if we regard metallic calcium as having the calcium fluoride structure with electrons replacing fluorine ions.

The explanation of this anomaly is to be found in a consideration of the dimensions concerned. In the sodium chloride lattice, for example, we imagine each negatively-charged chlorine (Cl^-) ion to attract its six neighbouring positively-charged sodium (Na^+) ions, until the attractive and repulsive forces counterbalance when the chlorine ion is in contact with its six neighbours. *Now this is only possible if the ions are of comparable size.* If the one ion is very

much smaller than the other, the closing-together process will be stopped, not by the contact of the unlike ions, but by the contact of the like ions of the larger size. In the simple case of the sodium chloride lattice, if r_1 and r_2 are the radii of the positive and negative ions, r_1 , being the greater, and if these are assumed constant in the case of contact between ions of like and unlike charges*, the critical value is clearly given by

$$\frac{2r_1}{\sqrt{2}} = r_1 + r_2.$$

If $\frac{2r_1}{\sqrt{2}} < r_1 + r_2$, then the closing-up process is stopped by

the contact of unlike ions; whilst if $\frac{2r_1}{\sqrt{2}} > r_1 + r_2$, the closing-

up process is stopped by the contact of like ions. In this way we may still adopt the point of view of the simple theory of the ionic lattice, and consider the oppositely-charged ions (or ions and electrons) as attracting one another, and yet understand why the resulting structures have such profoundly different properties in the two cases in which the closing-up process is stopped by the contact of unlike ions as in the simple salts, or of like ions as in the metals.

Now, if this conception be true, the possibility of finding relations between the interatomic distance in salts and metals at once arises. Any general relation is not to be expected for the following reasons. (1) It is by no means certain that the "radius" of an ion is the same when it is surrounded by different numbers of atoms in different orientations. (2) If the above picture of the metallic state is correct, the attractive forces pulling the atoms together are not always the same. Thus in sodium chloride the repulsion is between Na^+ and Cl^- ions, and acts against a direct electrostatic pull between the same two ions. But in a univalent face-centred cubic metal X the repulsion is between two X^+ ions, whilst the force holding those together is not a direct attraction between these ions, but is due to the components of the pulls due to the electrons, and the attractions will clearly be different if the face-centred atomic lattice has the electrons in different positions. Thus in the sodium chloride, zinc sulphide, and calcium fluoride structures the positive ions are all on face-centred cubic

* This assumption is, of course, really unjustified, and is only made to illustrate the way in which the argument applies to a definite structure.

lattices, but the positions of the negative ions vary. In the same way a given atomic lattice in a metal may correspond to different positions of the electrons, and the resulting attractions will differ. But in favourable cases with similar atomic arrangements relations may be traced. The work on the crystal structure of the alkali halides indicates very clearly that in these crystals the ions have radii * which are constant both when each is surrounded by six neighbours as in the sodium chloride type of lattice, and when surrounded by eight neighbours as in the caesium chloride type of lattice. Now, the alkali metals crystallize in the body-centred cubic structure, with each atom, or ion, surrounded by eight others, and we may reasonably compare these with the above alkali halides. The actual figures are shown in Table I. In order to avoid confusing the argument, the derivation of the ions in the halide crystals is given in a separate appendix.

TABLE I.

	Radius of metallic ion in salts.	One-half closest approach in metal.	Ratio.
Lithium	1.641 Å.	1.515 Å.	1.45
Sodium	1.257	1.86	1.48
Potassium	1.552	2.25	1.45
Rubidium.....	1.689	2.45†	1.45
Cæsium.....	1.974	2.64†	1.34

With the exception of caesium, for which the constants are imperfectly known, the interatomic distance in the metals bears a practically constant ratio to the diameter of the corresponding ions in the halide crystals, in complete agreement with the picture given above. The distances are of course greater in the metals, since here the ions in contact have similar charges and are only held together by the components of the attractions to the electrons.

We may now see how the above conception can be applied to the compressibility data of Bridgman. The simple dimensional argument used by the latter will still apply, since we are again using the conception of the crystal being

* Here, again, the term radius is not to be taken as implying a sharp boundary surface, but simply implies the distance at which the attractive and repulsive forces balance one another.

† These figures are derived from density determinations, as no direct X-ray measurements on the metal are available. The remaining figures are all from direct X-ray analysis.

built up by the attractions and repulsions of the different ions, and the simple argument does not consider which ions the repulsion is between, but merely places it as a function of the lattice constant, and considers the compressibility as being built up from the lattice constant and the electronic charge e . We should, however, expect the initial compressibility of metals $\left(\frac{1}{v_0} \frac{\partial v}{\partial p}\right)_{v=v_0}$ to be greater than that of

salts, since in the salts, where the attraction is between oppositely-charged ions in direct contact, the closing-up process (which is simply reinforced by external pressure) will clearly have proceeded further than in the metals, where the contact is between similarly charged ions, and the attraction is an oblique one towards the smaller electrons. This is, of course, in agreement with the facts. But the simple Born theory of the halide crystals will require modification before it can be applied to the metals, in order to take into account the fact that the particles are no longer held in contact by attractive and repulsive forces acting in the same directions and between the same particles. We can quite understand, therefore, that where, as in Bridgman's work, no such modification is made, the empirical values for the coefficient n of the repulsive force $\frac{b}{\delta^n}$ will be quite different in the metals and salts.

If the Born theory for the salts is applied directly to the metals without considering the above points, we should expect the empirical value of n , in the term $\frac{b}{\delta^n}$, to be less in

the metals, since here the contact is between the like ions where the electrostatic and non-electrostatic repulsions reinforce one another, and the repulsion, when expressed as a function of the distance, will be spread out more gradually; *i.e.*, n will be smaller in agreement with the facts. But for the theory to be applied strictly, it will be necessary to determine the position of the electron lattice, and to take into account the fact that the attraction and repulsion act in different directions between different particles, in contrast to the salts, where the attraction and repulsion are between the same particles. This would result in an alteration in the relative values of the constants a and b in the equation

$$\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n},$$

quite apart from the question of the validity

of a term of the type $\frac{b}{\delta^n}$. We are further able to understand why so many of the metals crystallize in one of the close-packed structures (cubic or hexagonal), the electrons occupying the "holes" between the larger atoms, since this will in general allow the closing-up process to proceed to its greatest extent, giving the least potential energy. This tendency is, in fact, shown by many of the gem-stones consisting of relatively large oxygen ions and small metal ions*.

The electron lattice theory therefore gives us a clear picture as to the way in which the crystal lattice is built up, and is in general agreement with the compressibility data, but before considering the other properties, it may be well to see how the other theories can be applied.

SECTION IV.

The principal difficulty with all the other theories is to see how the crystal lattice is built up. Generally speaking, crystals may be considered as being formed in three different ways. (1) There is first of all the simple ionic type of lattice described above. In some cases the ions are monatomic as in sodium chloride, whilst in others, such as calcium carbonate or sodium nitrate, they are more complex. Whatever may be the defects of the quantitative methods of Born, there can be no doubt that his theory gives a clear picture of the way in which these lattices are built up, and, as shown above, the same conception can be applied to the metals. (2) The second class of crystal may be regarded as formed by direct non-polar chemical combination of the atoms; *i.e.*, by the sharing of electrons between two or more atoms. An example of this kind of crystal is the diamond. The typical characteristics of this kind of crystal are hardness and brittleness, and usually high melting-point, although if the sharing involves much distortion of the orbits, the melting-point may be lower. (3) The third class of crystals includes the bulk of the compounds of organic chemistry; and here the crystal forces are regarded as being of magnetic origin. The molecules are considered to contain electrons spinning in opposite directions, and thus producing magnetic fields which tend to take up a definite orientation. The characteristics of this type are in general low melting-point and brittleness.

Now, if we adopt the Free Electron Gas theory, it is clear that the forces producing the crystal must be due to the

* See Bragg, Chem. Soc. Annual Reports, p. 275, 1926.

atoms (or ions) and not to the free electrons, which are, *ex hypothesi*, moving in all directions. Unless, therefore, we consider the crystal lattice as being produced in some quite unknown manner, we can only regard it as being formed by the sharing of the non-valency electrons or by the magnetic fields due to these. The softness and plasticity of the metallic crystals are definitely against the former supposition, whilst the plasticity and high melting-points of so many of the metals are against the latter. A similar objection applies to the theory of Wien and Gruneisen.

If the di-pole theory of Thomson is adopted, the difficulty is even greater, for here we have to allow for an actual movement of the atoms (or ions) in the crystal. It is difficult to see how this movement can occur if the formation of the crystal lattice is due to the sharing of electrons, or to the magnetic fields produced by oppositely spinning electrons, since both these conceptions require definite orientations of the atoms. In fact the only way in which it seems possible to reconcile the formation of a definite lattice by atoms free to revolve in that lattice, is to consider the free electrons as negative ions, and the lattice as an ionic one. In this case the theory is essentially that of the electron lattice, with the added assumption that the ions are electrical di-poles. As previously stated, such a marked degree of polarization appears improbable; it would, for example, lead us to expect a considerable electro-striction effect, analogous to magneto-striction.

We have already seen that the Bridgman theory distinguishes between two classes of metals—namely, those in which the conducting electrons pass through the atoms, and those in which they pass between the atoms. For the latter class of metals the theory differs little from the other theories which have been considered, but for the metals in which the electrons are regarded as passing through the atoms a different picture is required. This conception would seem to demand that the electrons are passing from one atom to another not merely when a current flows, but when the metal is not carrying a current; for, as pointed out by Bridgman, a motion through the atom with no resistance is only likely to occur in some kind of a quantized orbit or path. Unless this kind of motion exists before the current is passed, we should expect a discontinuous current-E.M.F. curve (analogous to ionization potentials) in place of the continuous Ohm's Law. But since the Bridgman theory requires the conducting electrons to be few (though constant)

in number compared with the atoms*, it is clear that we cannot regard these conducting electrons as producing the crystal lattice; and the formation of the lattice will again have to be regarded as due to the sharing of, or the magnetic fields produced by, the non-conducting electrons, which we have already shown to be improbable.

Of all the theories of the metallic state, therefore, the electron lattice theory is the only one which gives a rational explanation of the formation of the crystal lattice. It is not intended to deal here with the applications of the theory to alloys and metallic solid solutions, but we may note that the formation of the substitutional type of solid solution is more readily understood on the basis of the electron lattice theory than on any of the other theories; for the fact that substitutional solid solutions are formed by metals in which the ions have entirely different electronic structures (*e.g.*, copper and aluminium) appears incomprehensible if we regard the lattice as due to the orbits of non-valency electrons, but can be understood if we regard the lattice as ionic. We may now see whether the same theory is in agreement with the tensile properties of metals.

SECTION V.

(1) We may note in the first place that our picture is in some ways like that of the older crystallographers, who regarded the metals as built up of closely touching spheres. The difference is that whereas the older view regarded the spheres as held together by direct attraction towards the spheres themselves, the present view regards the "spheres" as mutually repulsive, and held in contact by attraction towards the interpenetrating electron lattice. Of course, the term "sphere" is not to be taken too literally. It merely implies that the ions are drawn together until the attractive and repulsive forces balance, and that any further closing-up involves entry into a zone in which repulsion predominates. It will be shown later that these zones of repulsion are probably not strictly spherical; but little error is likely to result in considering them as approximately spherical at ordinary temperatures, since the thermal oscillations will tend to obliterate the non-spherical characteristics, although at lower temperatures the non-spherical nature of the repulsive zones may become more pronounced. For the present, therefore, in representing the structure of metallic crystals, it will be

* We have already noted the improbability of this.

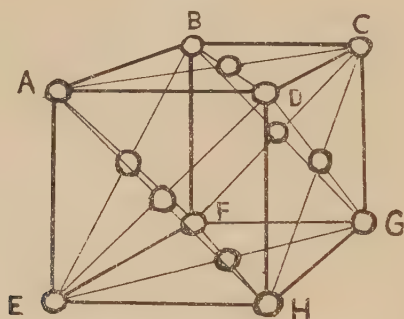
assumed that the ions are drawn into contact by attraction towards the electron lattice, and that the zones of repulsion can be represented by spheres of radius equal to half the closest distance of approach; *but this is not to be taken as implying the existence of any sharp bounding surface.*

It is at once apparent that this type of structure, in which comparatively large, mutually repulsive particles are held in contact by attraction towards much smaller particles interpenetrating the larger ones, is a structure very suited for plastic deformation when the larger particles are subjected to thermal oscillation and a stress is applied; for in the first place, as we have already shown, the great difference in the relative sizes of the positive ions and the negative electrons results in the structure being much less tightly bound together than in the case of the salts, where the ions are of comparable size (see page 1026); whilst, secondly, since the attractive forces between the atoms and electrons are of an electrostatic nature, we can understand their persisting after deformation has occurred, which is almost impossible if we regard the crystal forces as being directional in nature.

(2) We may consider first the case of the *face-centred cubic structure* in which so many metals crystallize. It is significant that three of the principal types of cubic salts, represented by the sodium chloride, zinc sulphide, and calcium fluoride types of lattice, all correspond to a face-centred cubic arrangement of cations; and so we can understand this type of lattice being formed by both uni- and di-valent metals. However we regard the electrons as being situated, we are to regard them as attracting the positive metallic ions until the latter are in contact. The closest approach is along the diagonals of the cube sides, the ions being in contact on the octahedral planes (cubical close packing). Further, whether we regard the electrons as occupying the positions of the chlorine ions in sodium chloride, of sulphur ions in zinc sulphide, or of fluorine ions in calcium fluoride, they will lie between the octahedral planes of the atoms. We have, therefore, a structure in which the relatively large metallic ions lie on close-packed octahedral planes, and it is clear that a glide or slip along an octahedral face is the type of motion which will take place most easily, and will cause the zones of repulsion of the ions to overlap least. Another way of looking at the matter is that if the deformation takes place by the ions rolling over each other, a slip on a octahedral plane will

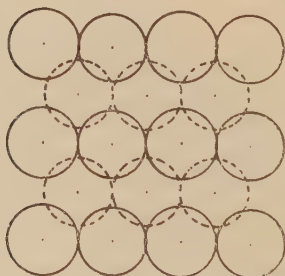
involve the least upward or downward motion. Fig. 2 shows a perspective view of the face-centred cubic structure, fig. 3 a view in the 110 direction, and fig. 4 a view in the 111 direction, which gives a direct plan of the octahedral faces.

Fig. 2.



The Face-centred Cubic Structure.

Fig. 3.

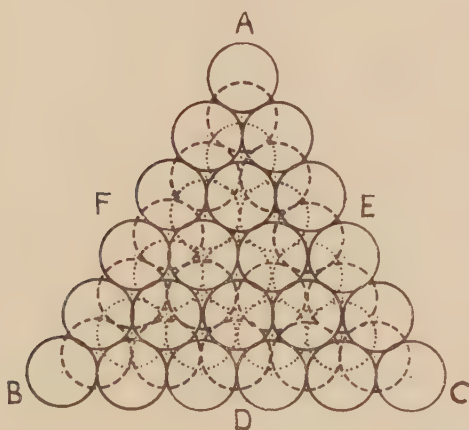


The Face-centred Cubic Structure: view in the (110) direction, *i. e.* at right angles to a plane such as A C G E in fig. 2. The first plane of atoms is shown in full circles, and the second in broken lines. The third is again directly behind the first.

When we inquire as to the direction in which slipping will take place in any one octahedral plane, we should again expect the direction in which the atoms are brought into least contact, which is clearly when the atoms in the one layer pass directly over the middle points of the lines joining the centres of the atoms in the next layer—that is to say, in the direction of a line such as AD in fig. 4. But if this is so, the slip on this individual plane cannot proceed by more than one unit or step in this direction, since the

triangular arrangement of the atoms or ions on these planes is such that, whilst the first step in this direction will bring the ions in one plane into least close contact with those in the next layer, the next step in the same direction will bring them into the closest contact, since the centres of the ions in the one layer will pass directly over, instead of between, those in the next layer. One possibility is therefore that the deformation will take place by single steps on a very large number of planes. For many reasons, however, it is probable that the units which slip in crystals are large compared with the interatomic distances, or, in other words, that slip continues on the planes on which it starts. This is

Fig. 4.

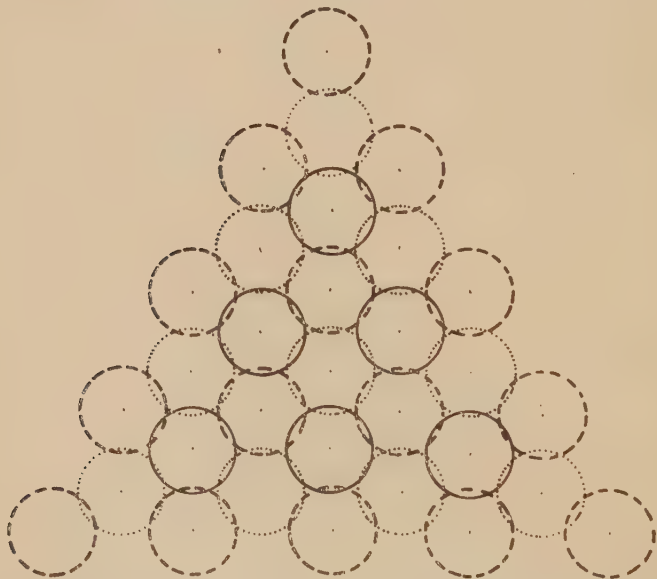


The Face-centred Cubic Structure: view in the (111) direction, *i.e.* along a diagonal such as DF in fig. 2. The first closely-packed layer is shown in full circles, the second in broken lines, and the third in dotted circles. The fourth layer is vertically under the first.

indicated by many facts, such as the comparatively small change in resistance, density, etc., produced by deformation. If this is so, it is clear that if this first step in the gliding on the particular octahedral plane is in the direction AD, the second step will have to be in one of the crystallographically similar directions such as BE or CF, after which a further step in the direction AD is possible, and will occur if the direction of the stress is unaltered, the process

repeating itself. The net result is therefore a motion in the direction of one of the sides of the triangle ABC, *i.e.* in the direction of one of the diad (110) axes lying in the octahedral plane; and this is the motion which will be observed, since any actual measurement involves a very large number of such steps. Out of the crystallographically similar alternatives, the particular octahedral planes and directions chosen for slip will be those for which the component of stress is greatest in the particular case. This kind

Fig. 5.

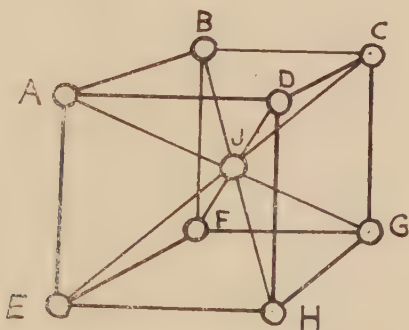


The Body-centred Cubic Structure : view in the (111) direction.

of motion in the (110) direction on the (111) plane is, in fact, that found by Taylor and Elam in the distortion of single crystals of aluminium, which crystallizes in the face-centred cubic system. This deduction in no way requires the ions to have a rigidly spherical shape, but depends on the assumption that gliding takes place so as to bring the ions into least close contact, and that slip continues on the planes on which it begins, the actual individuals out of innumerable parallel planes being determined presumably by slight flaws or inhomogeneities.

(3) We may next consider the hexagonal close-packed structure in which zinc, cadmium, magnesium, and other metals crystallize. This structure is very like the face-centred cubic, the difference being that in the close-packed layers each layer is vertically over the next layer but one, whereas in the face-centred cubic structure the repetition is at every fourth layer. Applying our previous argument, we should expect the gliding to take place along the close-packed layers in the same direction relative to these layers as before. This corresponds to motion on the basal plane in the direction of a closely-packed line of atoms, which is the exact kind of motion found by Mark and Polyani in the deformation of zinc crystals. In these two cases our deduction does not depend on giving the ions a rigidly

Fig. 6.



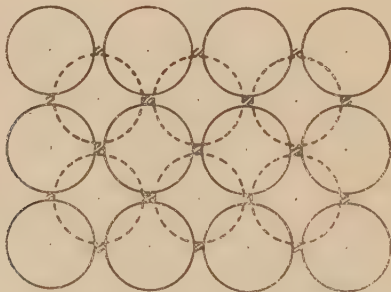
The Body-centred Cubic Structure.

spherical shape, but merely demands that they are drawn into contact along the directions of closest approach.

(4) The body-centred cubic structure may now be dealt with, since it is here that the results are most interesting. In this case we are in some doubt as to the position of the electrons. Symmetry conditions will clearly place them symmetrically in the centres of the cube edges or faces according as the metal is uni-, di-, or possibly tri-valent. In fact this seems the only way in which one or two electrons per atom can be symmetrically arranged. But if this is the case, the most densely packed layers, which are those of the rhombic dodecahedron, contain both ions and electrons, and we no longer have a case of close-packed atomic layers interleaved with planes of electrons. In these circumstances we find that an entirely different type of deformation is

possible. Fig. 7 shows a view of the body-centred cubic structure in the (100) direction. It is interesting to note that if the ions are assumed spherical, there are channels right through the structure*, and that an electron lattice could pass down these without "touching" the atoms, although the thermal oscillations will tend to obliterate this characteristic. Fig. 5 shows a view down the (111) axis. This last is very remarkable. Referring to the small sketch (fig. 6), the ion D and others in its plane are shown in full circles; the ions J and F appear vertically under D when we look down the (111) diagonal, and each full circle in the figure represents a vertical pile of ions in mutual contact. Ions A, C, and H are shown with broken lines, which again represent vertical piles, and ions B, G, and E are shown in

Fig. 7.



The Body-centred cubic structure; view in the (100) direction.

dotted circles, which once more represent vertical piles of ions. In the figure the zones of repulsion of the ions are drawn as spheres of diameter equal to the closest approach of the ions in the structure, which equals $\frac{a\sqrt{3}}{2}$ if a is the side of the cube. It can be seen that when looked at in this way the structure consists of a series of vertical piles of ions, and that each pile only very slightly overlaps the domain of the surrounding piles. We are thus led to the conclusion that in this structure deformation may result, not in the gliding of one plane over another, since closely-packed planes do not exist, but by the sliding of these long rows or piles of ions over one another, as though the structure consisted of bundles of rods. Improbable as this

* Reference to the literature showed that this point had been previously noted by Bridgman.

may at first sight appear, it is precisely the type of deformation which Taylor and Elam * were forced to assume as the only possible explanation of their results for the distortion of single crystals of iron, which crystallizes in the body-centred cubic structure. The exact words of these authors are as follows † : " The particles of the metal stick together along certain crystallographic directions, and the resulting distortion may be likened to a large bundle of rods which slide over one another." They showed further that the direction was that of a normal to a (111) plane, *i.e.* the (111) direction, just as the above reasoning indicated. This conclusion does not depend entirely on the assumption of rigidly spherical ions, but merely demands that the atoms occupy the positions of the body-centred cubic lattice, and that the zone within which the repulsion predominates is approximately that of the closest distance of approach in the unstrained structure.

On the other hand, in cases in which the zones of repulsion of the ions were markedly non-spherical, the above deduction would no longer be strictly justified, and movement in certain planes might be favoured.

If it is objected that the above treatment is really nothing more than the older method involving piles of spheres, it may be emphasized that the fundamental point in the present method is to consider the comparatively large atoms or ions as held in contact, not by attractions between each other, but by attraction to the much smaller electrons in between, and that a hard bounding surface is not being assumed. On the other hand, the electron lattice theory, and this theory alone, gives us justification for considering the atoms in metals as ions drawn together until a zone is reached in which repulsion predominates.

(5) We see, therefore, that the electron lattice theory, as interpreted above, is capable of predicting absolutely the type of deformation found for crystals of the face-centred cubic, body-centred cubic, and close-packed hexagonal structures. For the present it is not considered justifiable to carry the simple argument further. On the old assumption of closely-fitting spheres this could have been done, since the spheres were regarded as attracting one another, and a rolling-over process need not affect this attraction. But in the point of view adopted here the attraction is not between the "spheres," which are considered mutually repulsive, but between these and the interpenetrating

* Proc. Roy. Soc. A, cxii, p. 337 (1926).

† *Ibid.* p. 359.

electron lattice, and the deformation will clearly affect the relative position of the two lattices. It is clear that the mobility of the structure will be greatest at the exact equilibrium position where everything is symmetrical and balanced, and we can understand that any movement from this position with its resultant effect on the relative positions of the atomic and electron lattices will cause the attractive and repulsive forces to come into play so that hardening results. We can further see that change of temperature will act oppositely on the mechanical properties and the electrical conductivity. For in connexion with the deformation process, the chances of the comparatively large atoms, or rather ions, passing over one another will increase with the amplitude of their oscillations. But the electrical conductivity depends on the passage of the small electrons between the atoms, and thus takes place with little or no resistance at the absolute zero, although increasingly interfered with as the amplitude of the atomic vibrations increases.

(6) The fact that deformation produces so much more marked an effect on the hardness than on the electrical conductivity may now be referred to. In the first place it has already been noted that change of temperature acts oppositely on the electrical conductivity and the plasticity, and it may not be justifiable to compare these at the ordinary temperatures where the thermal oscillations have already reached a considerable magnitude. In the second place the deformation process depicted above involves the movement of planes or rows of ions which are in contact. If this is correct a comparatively small obstacle may hold up the movement of a large number of atoms. For example, in the type of deformation shown by iron, where the rows of ions glide over one another, a single obstacle at the end of a row will hold up the movement of a whole row, but it will only impede the passage of the electrons between the ions in the immediate vicinity of the obstacle itself. In this way the disorganization produced by a very small amount of slip may prevent further slip over a wide area, but may only affect the passage of the electrons between the ions over a small area.

It is doubtful whether any of the other theories of the metallic state can give such a complete picture of the deformation processes as the above, for they nearly all require, to a greater or less extent, that the forces producing the crystals are definitely orientated attractions between the atoms, which appear incompatible with plastic deformation.

On the other hand, the type of structure suggested above, with comparatively large mutually repulsive particles held in contact by attractions to much smaller particles, is admirably suited for the plastic deformation so characteristic of the metals.

The criticism of the electron lattice theory on the grounds of instability has lost much of its force in view of the recent discoveries of the remarkable properties of the single crystals of metals. In the case of aluminium* and copper, for example, the single crystals possess no elastic tensile strength at all at the ordinary temperatures, and in this sense it may be said that the single crystal is unstable.

SECTION VI.

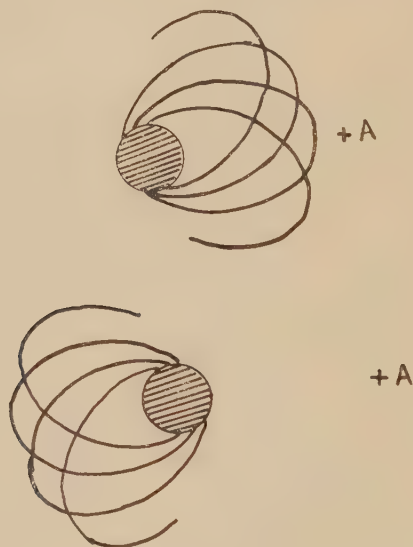
We may now discuss briefly the mechanism by means of which the electron lattice passes through the atomic lattice. We have noticed how in the comparatively open body-centred cubic structure there are channels straight through the crystal, if the ions are assumed spherical. In other structures this is not the case, and a more complex motion is required; but it may be emphasized that, although the positively-charged ions may be in "contact," there may still be room for the electrons to pass between them; for the zone of repulsion of a positively-charged ion for one of an opposite sign, or for an electron, will be smaller than its zone of repulsion for an ion of its own charge, on account of the opposing or reinforcing effects of the electrostatic charges in the two cases. It is therefore quite easy to understand how the electrons penetrate the ionic lattice, but it is not so easy to see how to reconcile the superconductivity motion at low temperatures with the conception of the formation of the lattice by the attractions of opposite charges. The explanation may perhaps be found in the nature of the ions themselves, and of the repulsive forces produced by their electrons. On the basis of the Bohr theory the electronic orbits are of two kinds, circular and elliptical. The circular orbits are comparatively simple, but the eccentric elliptical orbits are more complex. In that part of the orbit where the electron is far from the atom, the motion is that of a point charge moving round a massive nucleus. But when the electron comes round to the point where it is near to the nucleus, it plunges into the space occupied by the inner electrons, and undergoes a

* Phil. Trans. No. A, 636.

violent deviation from the simple motion. The result is a "central motion" which may be considered roughly as an elliptical motion with a violent precession of the major axis. Now up to the present we have regarded the repulsive fields of force of the ions as constant, but, strictly speaking, this would not seem correct.

Consider, for example, the effect of a single elliptical orbit at a point A as in fig. 8. It is clear that the position is very different at the different intervals of the precessional motion. We should therefore regard the spheres of repulsion of the ions, not as fixed, but as oscillating periodically. A motion

Fig. 8.



To show the effect of the precessional motion of the electrons upon the zones of repulsion of an ion.

of this kind may help the passage of the electrons between the atoms, just as, to give a crude illustration, a number of marbles may be pushed along a plane by a number of revolving elliptical cams. The motions of all the different ions will, of course, have to be in phase, and at ordinary temperatures this will be prevented by the thermal oscillations, which, however, die away as the temperature is lowered. A motion of this sort will be a kind of constitutional motion, distinct from the thermal oscillation, and its energy may correspond to the "Nullpunkt Energie" of the Quantum Theory which exists at the absolute zero

and cannot be given up. Whether the fundamental frequencies of the solids may be connected with a motion of this type is a matter which cannot be discussed here, but a conception of this sort seems to explain the way in which the electron lattice penetrates that of the atoms, and enables us to reconcile the conception of the ionic lattice with the fact of supra-conductivity.

It is to be noted that all metals do not show supra-conductivity at the temperatures of liquid helium, and in attempting to see which metals should show this effect on the basis of the above theory, the following factors have to be considered :—

(1) *The Crystal Structure.*—In general we should undoubtedly expect some structures to be more favourable than others. At present this point cannot be examined in detail owing to the lack of data for the crystal structures at very low temperatures, since the possibility of polymorphic changes makes it dangerous to argue from the structures at ordinary temperatures.

(2) *The Eccentricity of the Elliptical Orbits of the Ions.*—Here we should expect the effect of the precessional motion described above to be most marked in the case of the very eccentric orbits, or, in other words, in the elements of high atomic number, where the outer groups of electrons in the ions include the very eccentric 4_1 , 5_1 , or even 6_1^* orbits. This is quite in agreement with the fact that the elements which have been found to show supra-conductivity (indium, tin, mercury, thallium, and lead) are all of high atomic numbers.

(3) *The Symmetry of the Ion as a whole.*—In this connexion we should expect the above effect to be most pronounced where the ions in the metal were very unsymmetrical. Now, on the generally-accepted Stoner-Main-Smith modification of the Bohr theory, the first two electrons in a group form the N_{11} sub-grouping, and have the character of a more or less complete sub-group. On both chemical and spectroscopic grounds this is especially marked in lead and tin, and to a slightly less extent in thallium and indium. It is therefore highly probable that in these metals the whole of the valency electrons are not free, or ionized, in the solid metal, but that only those electrons which are not in the N_{11} groups are lost. In this case in tin and lead only two, and in indium and thallium only one, of the valency electrons will be free or ionized in the metal, and the

* See below for the case of lead and thallium.

resulting metallic ion will have a highly unsymmetrical structure such as $(60)(18)(2)^{++}$ for lead. It is, in fact, just these metals which show supra-conductivity.

On the other hand, the metals with symmetrical ions containing completed groups of 8 or 18 electrons, such as sodium, potassium, gold, silver, copper, zinc, and cadmium, do not show supra-conductivity, and neither do those in which the ions contain nearly complete 18 groups such as nickel and iron *; and we can quite understand that in a symmetrical ion with numerous similar orbits symmetrically disposed the above effect will be less pronounced. Mercury, however, is an exception to the above rule, if we regard the ion as having a structure $(60)(18)^{++}$ with two free electrons. Possibly this is connected with the other abnormalities of the mercury atom with its great reluctance to form the mercuric ion†; but whilst this particular point remains in doubt, it may be emphasized that the electron lattice theory as extended above is quite in agreement with the fact that some metals show supra-conductivity whilst others do not, since the factors (1), (2), and (3) just described will clearly vary greatly in different cases.

The electron lattice theory thus seems to have much to recommend it. It is in general agreement with the thermal and electrical properties, and in this connexion it can certainly hold its own with any of the rival theories. But in other connexions it seems to give a picture more comprehensive and more satisfactory than any of the other theories of the metallic state.

The author wishes to express his gratitude to Prof. Lindemann for his most kind interest and criticism.

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Oxford.

APPENDIX.

The Dimensions of Ions in Salts and in Metals.

In 1920 the conception of the constant radii of ions was first put forward by W. L. Bragg‡. The experimental evidence was that the substitution of one given cation for another in the alkali halides produced a practically constant change in the interatomic distances, irrespective of the nature of the anion, and similarly when one anion was

* For data see Onnes and Woltjer, Proc. 4th Int. Congress Refrigeration, i. p. 183 (1924); and Meissner, *Phys. Zeit.* xxvi. p. 689 (1925), *Z. Physik*, p. 38 (1926).

† The mercuric salts are almost unionized in solution.

‡ Phil. Mag. xl. p. 169 (1920).

substituted for another. The actual "radii," however, cannot be obtained from the interatomic distances, since however these are combined there is always one less equation than unknown quantity. The various methods of overcoming this difficulty are open to objection, since they involve assumptions either (as in the iron sulphide method) that the "radius" * of a positive ion in a metal is the same as in an ionized salt, which is certainly not true, or (as in the caesium di-chloro-iodide method) that the negative ions have the same radii in electro-valent as in co-valent compounds. These methods have been effectively criticized by Wyckoff †.

An alternative and more satisfactory method would appear to be as follows. The electronic configurations of the Cs^+ and I^- ions are identical (54 electrons), the only difference being that the nuclear charges are 55 and 53 in the two cases respectively. We may therefore as an approximation put the radius of these two ions as equal to half the distance between them in caesium iodide, and in this way obtain one more equation and so derive the whole of the radii of the different ions. The fact that the change in interatomic distance when one ion is substituted for another in both the caesium chloride and sodium chloride types of structure is the same, shows that we are justified in assuming that the "radii" of these alkali and halogen ions are the same when they are surrounded by either six or eight neighbours. In this way, using the interatomic distances given in Table II., we obtain the radii of the ions shown in Table III.

TABLE II.‡

Interatomic Distances in Å. in the Alkali Halide Crystals.

	F.	Cl.	Br.	I.
Li ⁺	2.007	2.566	2.745	3.015
Na ⁺	2.310	2.814	2.968	3.231
K ⁺	2.664	3.164	3.287	3.526
Rb ⁺	3.172?	3.286	3.434	3.663
Cs ⁺	3.015?	3.563	3.713	3.947

* The conventional term "radius" is used here, but of course this really only means the distance at which the attraction and repulsion balance, and does not imply a sharp surface.

† Proc. Nat. Acad. Sci. ix. p. 30 (1923).

‡ These figures are taken from work by Davey (Phys. Rev. xxi. p. 143, 1923) and Havighurst (J. Amer. Chem. Soc. xlvi. p. 2368, 1924). A critical selection has been made, and a mean value is taken where the two results appear of equal value. The differences are, however, very small. The value for CsF is from Wyckoff (J. Washington Academy Sci. xiii. p. 393, 1923).

TABLE III.

Ionic Radii deduced on the assumption that

$$\text{Cs}^+ = \text{I}' = 1.974 \text{ \AA}.$$

Li^+	$= 1.041$	
Na^+	$= 1.257$	$\text{F}' = 1.041 ?$
K^+	$= 1.552$	$\text{Cl}' = 1.589$
Rb^+	$= 1.689$	$\text{Br}' = 1.739$
Cs^+	$= 1.974$	$\text{I}' = 1.974$

From these tables it can be seen that the single assumption that the radii of the caesium and iodine ions are equal gives us within 0.05 \AA . the relations $\text{Rb}^+ = \text{Br}'$, and $\text{K}^+ = \text{Cl}'$. Unfortunately the results for the fluorine ion are uncertain, as for both caesium and rubidium fluorides there is a wide discrepancy between the densities calculated from the X-ray data and those obtained by direct measurement, and this point is not yet decided*. But the relation between the potassium and chlorine ions on the one hand, and the rubidium and bromine ions on the other, is one quite apart from the simple additive law, and very strikingly confirms the truth of the fundamental assumption.

Reference to the literature showed that a somewhat similar suggestion had previously been made by Davey †, who, however, made four independent assumptions: namely, that $\text{Na}^+ = \text{F}'$, $\text{K}^+ = \text{Cl}'$, $\text{Rb}^+ = \text{Br}'$, and $\text{Cs}^+ = \text{I}'$. In view of the fact that the relative difference in atomic numbers becomes greater as the atomic number decreases, and that the additive law itself holds more closely among elements of high atomic number, it would seem that the above method is more accurate.

TABLE IV.

Salts of uni- and di-valent ions of identical electronic structure, forming the same type of crystal structure.		Interatomic distance in the rock-salt type of structure.		Ratio.
KF	CaO	2.664	2.395	1.112
KCl	CaS	3.164	2.843	1.113
KBr	CaSe	3.287	2.957	1.112
RbBr	SrSe	3.434	3.117	1.102
RbCl	SrS	3.286	2.933	1.120
NaCl	MgS	2.814	2.539	1.108
NaF	MgO	2.310	2.09	1.105

* See Wyckoff (*ibid.*) for a criticism of this point for rubidium fluoride.

† Phys. Rev. xviii. pp. 102-104 (1921).

Additional support for this is found in the fact that where the rock-salt structure is formed by uni- and di-valent ions having the same electronic structure, *e.g.* sodium chloride and magnesium sulphide, the ratio of the interatomic distances is approximately constant, as is shown in the above table (Table IV.).

As pointed out in the above paper, the alkali metals crystallize in the body-centred cubic structure in which each atom is surrounded by eight others, and it is therefore justifiable to compare the interatomic distances in these with the dimensions of the ions deduced above. For lithium, sodium, and potassium direct X-ray data are available, but not for rubidium or caesium. In papers by Bridgman on the effect of pressure on electrical resistance, the results are taken to indicate that rubidium and caesium have the body-centred structure: and on this assumption the interatomic distances can be calculated from the densities, since if a is the side of a unit cube (in Å.),

$$a^3 = \frac{K \times \text{atomic weight}}{\text{density}}.$$

For lithium, sodium, and potassium the values of K are 3.28, 3.35, and 3.10 respectively (from the X-ray data and densities), and taking a mean value of 3.24, we find the closest distances of approach to be 4.90 Å. for rubidium (density 1.53) and 5.28 Å. for caesium (density 1.90). Theoretically these values for K should be constant, and could be calculated, the differences being due chiefly to errors in the density determinations. But as these errors are likely to be in the same direction for all the alkali metals, it is thought better to use the above mean value. We have, therefore:

TABLE V.

	One-half closest approach in metal.	Radius of ion in halides.	Ratio.
Lithium.....	1.515 Å.	1.041 Å.	1.45
Sodium	1.86	1.257	1.48
Potassium.....	2.25	1.552	1.45
Rubidium	2.45	1.689	1.45
Caesium	2.64	1.974	1.34

With the exception of caesium, for which the constants are imperfectly known, the constancy of the ratio is very striking.

XCVI. *On the Application of the Aitken Effect to the Study of Aerosols.* By HENRY L. GREEN, M.A. (Cantab.), A.Inst.P. *

[Plate XXII.]

Introduction.

FOR the quantitative study of a disperse system in air or, as it has been more generally termed, an aerosol, a knowledge of the number of particles existing at any time is of fundamental importance.

Several methods have been employed for the accurate counting of the particles in dusts, smokes, and similar systems. Aitken † determined the number of "dust" particles in air by condensing moisture on them and counting the water-droplets thus formed, after they had settled on a glass plate. Whytlaw-Gray and others ‡, using a slit ultra-microscope of the Zsigmondy-Siedentopf type, made direct counts on the number of particles in smokes, and were able to follow the changes taking place during rapid coagulation. It was realized, however, that the method was subject to certain limitations; amongst others, the limit of smallness of particle which could be seen depended upon the particular optical system used and the sensitiveness of the retina of the observer. At the time when their experiments were carried out it was thought that many amicroscopic particles existed in the smokes that were examined. With the view to extending the range of the ultra-microscope the idea has been developed of combining Aitken's method, which is capable of revealing particles of exceedingly small dimensions, with that used by Whytlaw-Gray.

Aitken § found that, when moist air is cooled by a rapid expansion, water will condense into droplets only if there are nuclei present for their formation and the degree of supersaturation attained has been sufficiently high. This effect has been termed, for the purpose of this paper, the "Aitken" effect. His apparatus in its original form is not directly adapted for the continuous examination of aerosols, which may be rapidly coagulating, but the form of rapid expansion apparatus developed by C. T. R. Wilson || can be

* Communicated by the Author.

† Collected Scientific Papers of John Aitken. Ed. by C. G. Knott, p. 187.

‡ R. Whytlaw-Gray, J. B. Speakman and J. H. P. Campbell, Proc. Roy. Soc. A, cii. p. 600 (1923).

§ *Loc. cit.* p. 199.

|| C. T. R. Wilson, Proc. Roy. Soc. A, lxxxvii. p. 277 (1912).

used successfully for producing expansions in the cell of an ultra-microscope, and the water-droplets formed by condensation on nuclei, such as are provided by the particles in a smoke, can be counted. For the more accurate counting of the droplets a photographic method in conjunction with a mechanical type of Wilson apparatus has been developed, and it is the purpose of this paper to describe this method and to show how it has been applied to the study of certain smokes.

Before dealing with the experimental methods in detail it is desirable to discuss the theoretical considerations underlying the application of the Aitken effect.

Theoretical Considerations.

The theory of the application of the Aitken effect has been worked out in detail by C. T. R. Wilson * ; here, the theoretical aspects have been merely summarized and data calculated in accordance with the particular experimental conditions holding in this investigation.

If air, saturated with water-vapour, is subjected to an adiabatic expansion of a given ratio, *i. e.* becomes supersaturated to a given degree, moisture will condense round any nuclei present, provided they are larger than a certain size.

Now there is a relationship between the minimum radius of an uncharged droplet, which could exist and grow, and a given degree of supersaturation which is expressed by the equation developed by Kelvin † and applied by Helmholtz ‡ to the case of droplets ; Kelvin's equation is

$$\log_e \frac{p_1}{p_2} = \frac{2S}{RT\rho r}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p_1 is the vapour-pressure over droplet, p_2 the vapour-pressure over a plane surface, $\frac{p_1}{p_2}$ the degree of supersaturation, S the surface-tension of liquid, r the radius of droplet, R the gas constant, T the absolute temperature, and ρ is the density of the liquid.

But a droplet will not form even with this supersaturation unless a nucleus of at least the same radius is present. So that it is possible to calculate the minimum size of uncharged

* C. T. R. Wilson, *Phil. Trans. A*, clxxxix. p. 265 (1897).

† Kelvin, *Proc. Roy. Soc. Edin.* vii. p. 63 (1870).

‡ K. R. von Helmholtz, *Wied. Ann.* xxvii. p. 508 (1886).

nuclei which must be present in order to produce a cloud of droplets with a given degree of supersaturation.

Now in an adiabatic expansion,

$$v_1\gamma^{-1}\theta_1 = v_2\gamma^{-1}\theta_2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v_1 is the volume before expansion, v_2 the volume after expansion, θ_1 the temperature before expansion, θ_2 the temperature at instant after expansion, and γ is equal to C_p/C_v .

Therefore, given the volume change, the theoretical instantaneous lowering of temperature can be calculated and the degree of supersaturation existing found after reference to vapour-pressure tables (see Column IV., Table I.).

From this value and by using the Kelvin equation the minimum sizes of uncharged nuclei for the formation of droplets have been derived (see Column V.). It must be noted that, in order to make these calculations, it is necessary to assume that the gas laws may be applied to water-vapour.

To gain an idea of the size of droplets formed it is necessary to calculate the mass of water deposited after a given expansion. When condensation takes place the process will continue until the heat liberated causes the temperature to rise to an equilibrium value and the remaining water-vapour is just saturated. Under these conditions

$$L(\rho_2 - \rho_3) = MC_v(\theta_3 - \theta_2), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where L is the latent heat of water at the mean temperature, ρ_2 the density of water-vapour at temperature θ_2 , ρ_3 the density of water-vapour at equilibrium temperature θ_3 , M the density of moist air at the same temperature, C_v the specific heat of air at constant volume, θ_3 the equilibrium temperature, and θ_2 is the temperature at the instant after expansion.

The point of intersection of the curve given by this equation (derived values of ρ_3 being plotted against given values of θ_3) with the curve for the variation of density of water-vapour with temperature must give the values of ρ_3 and θ_3 attained for a given expansion, *i. e.* given value of θ_2 . The difference between ρ_2 and ρ_3 gives the mass of water deposited per c.c. (see Column VI.).

For the purpose of detecting particles in aerosols an expansion ratio greater than about 1.38 probably cannot be used, since a general cloud is formed for expansions greater than this, even with perfectly dust-free air. In the case of smokes it is hardly necessary to use an expansion ratio

TABLE I.

Initial Temperature Expansion Ratio.	Initial Temperature 15° C. Instantaneous Temperature. °° C.	Initial Pressure Equilibrium Temperature. °° C.	760 mm. Hg. Degree of Super- saturation.	Radius of Nucleus revealed. cm.	Mass of Water condensed. gm./c.c.	Radius of Droplets. cm. (Water divided amongst 10 ⁷ particles/c.c.).
1.05	9.5	13.0	1.34	3.89×10^{-7}	0.94×10^{-8}	2.86×10^{-5}
1.10	4.1	10.6	1.84	1.33×10^{-7}	2.07×10^{-8}	3.67×10^{-5}
1.15	0.7	8.7	2.40	1.38×10^{-7}	2.80×10^{-8}	4.06×10^{-5}
1.20	-5.4	6.2	3.25	1.05×10^{-7}	3.38×10^{-8}	4.32×10^{-5}
1.30	-13.8	2.2	5.56	7.55×10^{-8}	4.28×10^{-8}	4.67×10^{-5}
1.40	-21.4	-1.9	9.05	6.14×10^{-8} *	4.91×10^{-8}	4.90×10^{-5}
1.50	-28.4	-5.5	13.80	5.37×10^{-8} *	5.29×10^{-8}	5.02×10^{-5}
1.60	-34.6	-9.2	20.05	4.86×10^{-8} *	5.57×10^{-8}	5.10×10^{-5}

* It is probable that the Kelvin formula no longer holds for droplets formed with these expansions owing to the variation of surface-tension, when the diameter of droplet becomes very small.

All physical data have been taken from the Smithsonian Tables (1918).

approaching this value. At a ratio of say 1.30, if the theory holds, a spherical uncharged nucleus 7.55×10^{-8} cm. in radius should be detectable at $15^{\circ}\text{C}.$; actually, particles in smokes are not necessarily spherical and many may be electrically charged, but these factors would tend, practically in every case, to favour deposition of water-vapour. The case in which charged particles of very small dimensions would not be revealed was not likely to arise in connexion with any of the aerosols it was desired to investigate by this method.

If the water deposited at the expansion ratio 1.30 were equally divided amongst 10^7 nuclei per c.c. (a number far greater than that attained in any aerosol so far examined), droplets of radius of the order 4.67×10^{-5} cm. would be formed. This size is well within the range of the ultra-microscope. It would be expected, however, that the water-droplet clouds would be heterogeneous since nuclei of different sizes would probably condense water at different rates.

The Visual Method of Counting.

The method of directly counting particles in aerosols was based on that developed by Zsigmondy for obtaining the number of particles in colloidal solutions. The original procedure adopted by Whytlaw-Gray was to pass a slow stream of the aerosol through an ultra-microscope cell illuminated by a beam of light of known depth. The particles were viewed through a microscope in which the field of vision was cut down by a square diaphragm in the eyepiece, so that the number of particles seen at any moment could be estimated at a glance; most observers find it difficult to estimate with accuracy more than six to eight particles in the field at once. Fifty instantaneous counts were taken on the slowly moving stream. The arithmetic mean of these counts multiplied by a factor, calculated from measurement of the volume of aerosol viewed, gave the number of particles per unit volume.

The above method, which formed the basis of the procedure for counting water-droplets produced by the condensation of moisture on the particles of a cloud, suffered from the defect that particles or droplets outside the beam of light, faintly illuminated by scattered or reflected light from those within the beam, were liable to be counted. This was pointed out in the first instance by Whytlaw-Gray, and he explains the high values he obtained for his original number counts as

being due to counting particles outside the beam, *i. e.* to an under-estimation of the effective depth of the beam.

Hence it is evident that this particular visual method of counting the droplets can only give roughly quantitative results, although relative values may be fairly accurate. It was decided, therefore, to develop a method of photographing the droplets formed in a mechanical or continuous-action Wilson apparatus and of counting their images on the negative with a low-power microscope. It was considered that there would be sufficient contrast between droplets within the beam of light and those without, to enable differentiation to be made in counting on the photographic plate. Further, a much deeper beam could be used, enabling more droplets to be counted and more observations to be taken in a given time.

Before giving an account of the photographic method a brief account will be given of the visual method, as this has a certain quantitative value.

Adiabatic expansions were obtained by the well-known plunger method due to Wilson*. An expansion chamber, diameter $2\frac{1}{2}$ cm., was connected directly to an ultra-microscope cell $\frac{1}{2}$ cm. in diameter and 3 cm. long, similar to the one used by Whytlaw-Gray†. A vertical scale was fixed to the expansion chamber so that the height of the plunger could be read; the apparatus was calibrated and a given height of the plunger corresponded to a certain expansion ratio. Wherever possible, the cell was lined with damp blotting-paper to keep the air inside thoroughly saturated with water-vapour.

The apparatus was mounted on a bench ultra-microscope of the slit type, a 1000-c.p. pointolite lamp being employed as the source of illumination. In using the apparatus, the plunger was roughly adjusted to slightly below the position to give the desired expansion, and a sample of the aerosol to be examined was drawn in by aspiration. The height of the plunger was then finally adjusted to the required height and all taps were shut. After an interval of 30 seconds, to allow the air to become saturated, the expansion was made. With air containing particulate matter a cloud would be formed and the droplets could be seen falling in the field of view. By using a sufficiently shallow beam and a suitable diaphragm the number of droplets in the field of view could be cut down, so that, as they fell, the number at any instant

* C. T. R. Wilson, *loc. cit.*

† R. Whytlaw-Gray and others, *loc. cit.*

could be estimated. At least 25 counts could be made before there were any signs of evaporation. Hence two expansions were usually made to give 50 counts, which were averaged and the number of particles per unit volume deduced.

Apart from the errors inherent in the ultra-microscope itself, there were possible errors arising from the difficulty in counting droplets moving rather rapidly through the field of vision. These errors would be particularly noticeable when there were a large number of droplets in the field, and when there were very few, with numerous "blanks" appearing in the counts. A continuous-action Wilson apparatus, which obviated these errors, was designed; subsequently it was used for the photographic method, for which an easily operated mechanical type of apparatus was essential.

A Continuous-Action Wilson Apparatus.

In this apparatus, the idea has been to arrange for a continuous series of expansions each on a fresh sample of the cloud; one count or photograph only is taken, immediately after the completion of each expansion, when the droplets are retained for the moment stationary in the field.

There were several necessary features which had to be borne in mind when the apparatus was designed. Expansions had to be very rapid, if not adiabatic, means had to be provided for changing the sample of aerosol after each expansion so as to guard against any possible diminution of numbers due to falling out of particles, and further, it was necessary to arrange for a pause in the action of the apparatus, just after the expansion, to enable a count or photograph to be taken.

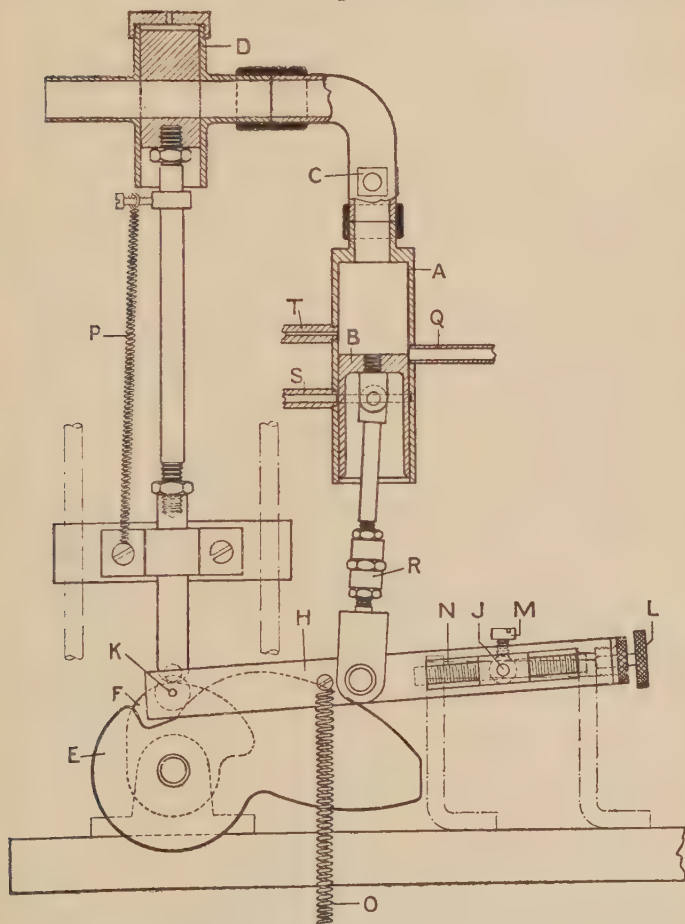
A diagram of the apparatus is shown in fig. 1.

Expansions were caused by the motion of the piston (B) working in the cylinder (A). To the cylinder is attached by a rubber connexion an ultra-microscope cell (C), which in turn is connected to a shut-off valve (D). The motions of valve and piston are controlled indirectly by two cams (E) and (F) working on the same spindle, which is rotated by a 1/20 H.P. electric motor geared down through a gear-box (gear ratio 1:64).

The piston is linked with the rocker-arm (H), one end of which pivots at J and the other rests on the cam (E) through the roller (K). The pivotal point can be moved by the screw (L) so as to alter the length of the stroke of the piston and therefore the expansion ratio, as in the Ray Track

Apparatus evolved by Shimizu*. In addition to turning the screw when altering the length of the stroke, it is necessary to adjust the position of the pivotal points so as to maintain the roller (K) always in the same relative position with regard to the cam. This is done by slackening the

Fig. 1.



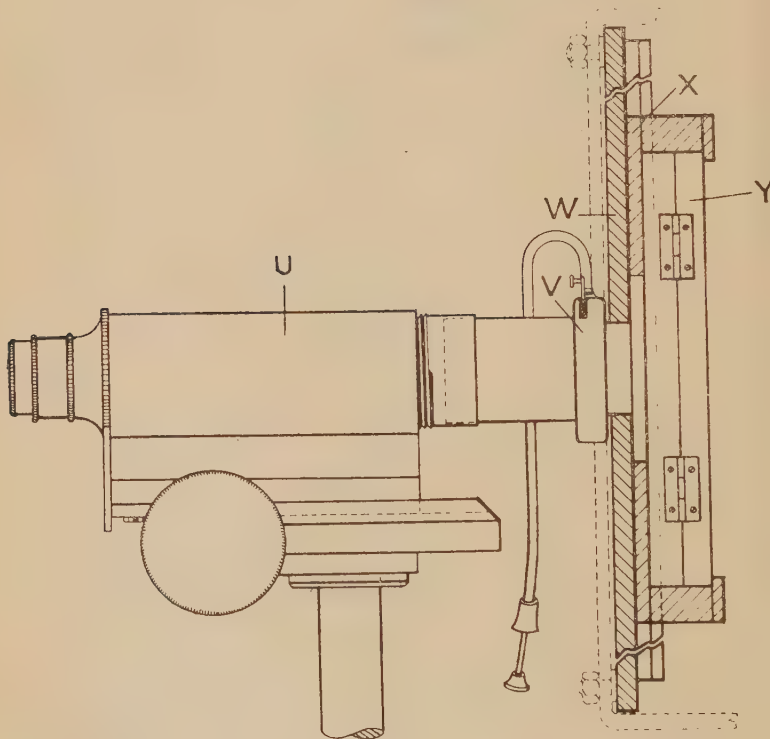
screws (M) and (M1—not shown in diagram), and moving the pivot with the rocker-arm along the parallel bars (N) and (N1—not shown in diagram) to its required position and tightening the screws once more. A long powerful spring (O) keeps the rocker-arm bearing on the cam (F), whilst a

* T. Shimizu, Proc. Roy. Soc. A, xcix. p. 425 (1921).

second spring (P) keeps the slide of the shut-off valve bearing through its stem and roller on the other cam.

The apparatus was mounted with the ultra-microscope illuminating system and viewing microscope mutually at right angles, the axis of the latter being set in the same plane as the cell and cams shown in the diagram.

Fig. 1 (continued).



Action of Apparatus.

In practice the slide-valve was connected through about 40 cm. of glass tubing, diameter 1 cm., lined with damp blotting-paper, to the chamber containing the cloud, and the cylinder connected through the port (Q) to an aspirator. The cell was also lined with damp blotting-paper. The action of the apparatus is best described by tracing what happens during one revolution of the cams.

Consider the cams in the position shown in the diagram, when the port in the cylinder is uncovered and the shut-off valve is open. A sample of the cloud is being drawn through, and as the cams rotate the piston rises, shutting off the suction, the valve, however, remaining open. Just as the piston reaches its topmost position the valve shuts, and almost immediately afterwards the piston drops very suddenly, causing an almost adiabatic expansion of the air in the cell and cylinder; the roller of the rocker-arm falls on the circular portion of its cam. As the cams continue to rotate both valve and piston remain stationary, thus enabling a count to be taken of the droplets formed by condensation of moisture on any particles present. The valve now re-opens, and the piston drops, uncovering the port, and the cycle is thus started again. One revolution takes two seconds, and thus 50 counts are completed in 100 seconds.

In actual practice, certain difficulties, which were successfully overcome, were experienced with the apparatus. Leaks round the valve and piston were prevented by maintaining a film of castor oil over the working surfaces. In the case of the valve, a little oil was poured on the top of the slide from time to time and this was sufficient to keep the valve air-tight in its closed position. A reservoir of oil, feeding through the copper tube (S) on a ring cut in the walls of the cylinder below the port, maintained a film of oil on the piston and kept it air-tight.

The motion of the droplets after expansion was a source of considerable trouble. Partly owing to the peculiar construction of the cell and partly to convection, the droplets commenced to move downwards with a velocity greater than their terminal velocity immediately after each expansion, although the apparatus was perfectly air-tight. An upward current of air of suitable velocity would keep the droplets stationary. It was found that this could be obtained by allowing air to leak into the cylinder at a controlled rate after the rapid expansion had been completed. Accordingly a copper tube (T) of capillary bore, to which was attached a piece of rubber tubing and screw clip, was let into the cylinder. By regulating the screw, air could be admitted into the cylinder at a rate sufficient to correct the downward movement of the droplets in the ultra-microscope cell and cause them to remain stationary long enough for a single count to be made in the usual way.

There were two reasons for retaining the narrow cell :

- (a) The beam of light had only to pass through a small length of cloud before being brought to a focus ; thus losses of light due to absorption or scattering were reduced to a minimum.
- (b) The beam could be brought quite close to the front of the cell so that there was little "fogging" of the illuminated droplets by droplets between the beam and the objective.

The apparatus was calibrated for a particular expansion ratio by first of all determining the pressure change with a manometer connected to Q, when the piston was allowed to drop from its highest position to its lowest position, *i. e.* to the position where the port is uncovered, the valve (D) being kept shut. The actual pressure change was measured by a null method—that is by determining to what pressure the air in the tube (Q) must be adjusted in order that the manometer should show no change when the tube was opened to the cylinder after the expansion.

The internal diameter of the cylinder and the stroke of the piston, when the roller (K) fell to its various positions on the cam, were measured, and hence the pressure change could be calculated for the normal case when the roller dropped to the circular part of the cam. From this value and the value of the saturation pressure of water-vapour in the apparatus the expansion ratio was easily calculated.

Visual counting with this apparatus was found to be much easier and more accurate than with the earlier type. The adaptation of the apparatus for the photographic method is given below.

The Photographic Method of Counting.

Experiments have been carried out with various lens systems, plates and sources of illumination. The eventual arrangements evolved are as follows :—

The continuous-action Wilson Apparatus was set up in conjunction with the bench ultra-microscope and a 10 ampere Zeiss arc, with automatic feed, as source of illumination. The vertical reading microscope (U), normally used for counting, was arranged to throw an image of the droplets (magnification about $\times 2$) on the photographic plate. In order to do this, the 1-inch objective was replaced by one of $2\frac{1}{2}$ -inch focal length and an extensible tube, in place of the draw-tube and eyepiece, connected the microscope to a self-capping shutter (V), which was attached to a fixed

panel (W). A movable panel (X), holding a quarter-plate dark slide (Y), fitted into vertical grooves in the fixed one, thus permitting up and down movement of the plate. The slide could also be moved laterally so that, without undue crowding, it was possible to secure seven columns each of fourteen photographs on the one plate.

The procedure adopted has followed the same lines as in making visual counts except that a photograph could be taken of, practically speaking, the whole illuminated field, when, in the ordinary way, a count on only a very small portion could be made. By careful adjustment of the air-leak in the Wilson apparatus it has been possible to keep the droplets sufficiently steady after the expansion to allow an exposure of as much as one-fifteenth of a second to be made. The exposure is made by hand, but there is no difficulty in judging the moment when the shutter should be released. Ilford "Monarch" plates have been found quite satisfactory for this work.

A platinum wire was looped round the windows of the cell and maintained at just a sufficient temperature by an electric current to prevent condensation of moisture on them. The heat from the wire has a tendency to set up convection currents in the cell, but the number of photographs spoilt due to this cause is comparatively few. The top of the cell could be water cooled, if necessary, in order to slow down evaporation when the room temperature was high.

In Plate XXII. is shown a series of specimen enlargements of photographs taken during the history of an ammonium chloride cloud. The total magnification is $\times 23$, *i.e.* the magnification of the original photographs is $\times 5$, and the depth of the beam at its focus, 0.0263 cm.

The images of the droplets were counted on the photographic negative under a microscope using a $1\frac{1}{2}$ -inch objective and a $\times 4$ eyepiece, which gave a total magnification of about 20 diameters. A graticule ruled into 100 squares was set in the eyepiece. Only images in the central portion of each photograph were counted; these were of droplets within the beam of light and the depth of focus of the photographing objective, which gave clearly defined images. Droplets outside the beam illuminated by scattered light gave fainter images than those fully illuminated. These were comparatively few in number, and it was a matter of judgment whether or not they should be included in the counts. The magnification was such that the images covered by 24 (6×4) to 40 (4×10) squares in the graticule could be counted, just in the same way as the

ordinary ultra-microscope counts are taken with a square diaphragm. The counts from a number of successive photographs were averaged and multiplied by a factor to give the number of particles per c.c. in the cloud. The factor was obtained after calibration of the microscope and photographing objective, and determination of the expansion ratio in the Wilson apparatus and the depth of the beam of light.

Since the beam of light in the cell is shallower at the centre than at the sides, the depth was carefully measured over the whole area in which counts were made. This was done by turning the crossed slits through a right angle and taking photographs under the same conditions as in actual experiments. The depth was then measured on the plate by means of a reading microscope. It was necessary to take the mean of a number of readings on different photographs, as the confines of the beam are not *absolutely* sharp and there is a slight variation between one photograph and another.

A mean depth of as much as 0.5 mm. could be used, but, when the cloud contains a large number of particles, it is convenient to use a shallower beam, thus reducing the number of droplets photographed and preventing overlapping of images.

It is estimated that the various steps in the calibration may cause a total error in the calibration factor of as much as ± 10 per cent.

With the present apparatus a photograph can be taken at every revolution of the cams, *i.e.* every two seconds, and aerosols containing from 3×10^4 to 3×10^6 particles per cubic centimetre can be examined with it. An example of actual measurements in calibration is given below :—

Minimum depth of beam of light	=	0.0263 cm.
Mean depth of beam over area on photographic plate in which counts were made	=	0.0382 cm.
Area of plate covered by one graticule square of counting microscope	=	(0.043) ² sq. cm.
Magnification of photographing objective	=	2.44.
For each photograph counts were made from 10 × 4 graticule squares.		
Hence volume of cloud in Wilson apparatus in which counts were made	=	$\frac{40 \times (0.043)^2 \times 0.0382}{(2.44)^2}$ c.c.
Expansion ratio of Wilson apparatus	=	1.406
Therefore actual volume of cloud in which counts were made	=	$\frac{40 \times (0.043)^2 \times 0.0382}{(2.44)^2 \times 1.406}$ c.c.
Hence factor to convert number of particles per 40 counts to number of particles per c.c.	=	$\frac{(2.44)^2 \times 1.406}{40 \times (0.043)^2 \times 0.0382}$ = 2.97 × 10 ³ .

*Application to the study of Ammonium Chloride
and Cadmium Oxide Clouds.*

Whytlaw-Gray and others * have studied various types of smokes of a high degree of dispersion and established that the initial rapid fall in the particulate number curves is due almost entirely to the coalescence of particles. In some of their subsequent work he and his co-workers have come to the conclusion that, owing to the inherent defects in the ultra-microscope itself, their original particulate number values were too high. They have since evolved a type of ultra-microscope cell which does not suffer from these defects, and by means of which they have made a fresh series of counts on ammonium chloride and cadmium oxide clouds. The application of the Aitken effect provides an independent means of counting the total number of particles and determining the rate of coagulation of such clouds.

Clouds were dispersed in an air-tight metre cube made of glass set in a wooden framework, which could be rendered dust-free by blowing through filtered air for about an hour.

The first series of determinations was made with ammonium chloride clouds. It was decided to disperse the substance under conditions which should be as simple as possible. Clouds were generated by comparatively slow sublimation from a platinum boat shaped to fit on a quartz U-tube, heated electrically. The heating element was a spiral of nichrome wire threaded through the tube and raised to a red heat by a current of about 1.6 amperes. The U-tube was sealed to glass tubes which carried the leads to the wire outside the chamber, so that no nuclei from the wire itself could reach the inside of the chamber. No nuclei were shot off by the boat or U-tube, and it was therefore possible to generate clouds, containing particles which were initially uncharged, in dust-free air. In no case was the air in the chamber dried, but was left at the ordinary humidity of the atmosphere.

The weight of ammonium chloride in the boat before an experiment was always the same, the amount sublimed being controlled by the length of time during which the boat was heated; this varied from one to three minutes according to the concentration desired. A fan set opposite the U-tube and about 12 inches from it was kept running for five minutes after the commencement of generation of the cloud.

The continuous-action Wilson apparatus was connected to the chamber as previously described. The expansion ratio

* Whytlaw-Gray and others, *loc. cit.*

was kept as high as 1.406, since it was necessary to make certain that all the particles were being revealed. As the expansions were not truly adiabatic this was below the limit of general cloud formation. With the plunger type of apparatus it was found by direct experiments that an expansion ratio of 1.10 will reveal all the particles in these aerosols. It was also possible to show by a direct comparison that the continuous-action Wilson apparatus was revealing all the particles.

Probable Errors of Observations.

The question of how many particles must be counted in order to deduce a reliable value for the number of particles per c.c. in the cloud at any time is considered in the case quoted below.

Three photographs were taken at intervals of two seconds of different samples from an ammonium chloride cloud in its initial stages. Forty counts were made from each photograph and the numbers of occurrences of 0's, 1's, 2's, etc., per square of the eyepiece graticule were plotted against their respective numbers. The curve (fig. 2) is a smooth and typical probability one. By applying the ordinary probability formula the probable error of the arithmetic mean of any forty observations was calculated. This amounted to ± 4.40 per cent., the average per square of the graticule being 5.37.

The probability that there should be n particles per square is given by $\frac{x^n}{n!} \cdot e^{-x}$, where x is the average number per graticule square and n may have any positive value from 0 to ∞ . Observed and calculated number of occurrences are given below :—

Average number per graticule square : 5.37.

Number of particles per graticule square :

0	1	2	3	4	5	6	7	8	9	10	11	12.
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Observed number of occurrences :

0	7	6	13	16	24	23	14	7	5	3	2	0.
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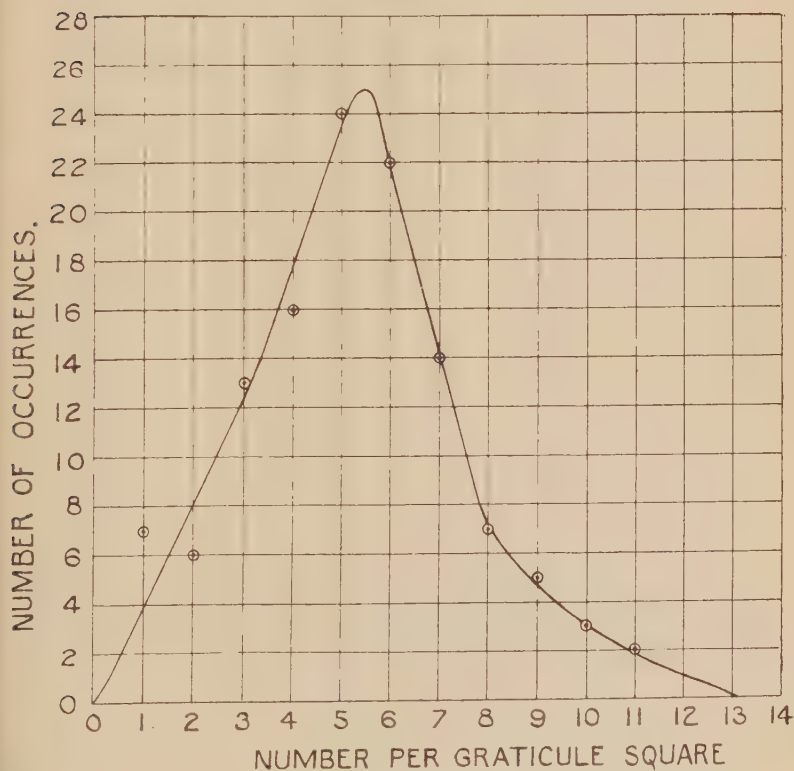
Theoretical number of occurrences :

1	3	8	14	19	21	19	14	10	6	3	1	1.
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The agreement between the sets of figures is good, considering the small number of observations that were taken.

This procedure has been carried out for a number of clouds and in every case the theory of probability has been shown to hold. It appears therefore that the variation in individual counts, and in the average of forty counts between successive photographs, is such as would be expected from the random distribution of particles, and is not due to any inhomogeneity of the cloud, any fluctuation in its behaviour or in the action of the apparatus.

Fig. 2.



In order to deduce the number of particles in a cloud at any mean time sufficient photographs are taken to enable some five hundred droplets to be counted, thus reducing the probable error of the observation to ± 3 per cent. This convention has been adhered to in most of the subsequent work with the apparatus.

Results for Ammonium Chloride.

A number of clouds of various concentrations was dispersed by the method described, and their histories followed for about an hour and a half. The detailed figures for a typical cloud are given below and shown graphically in fig. 3. Enlargements of photographs taken from the negative for this cloud were shown in Plate XXII.

TABLE II.

No. of Photographs.	No. of Particles Counted.	Mean Time.	No. of particles per c.c. $n \times 10^{-5}$.	Particulate volume $1/n \times 10^5$.
		min. sec.		
3	592	6 40	5.86	0.171
4	667	9 5	4.95	0.202
4	523	15 15	3.88	0.258
5	558	19 30	3.34	0.302
6	559	27 35	2.76	0.362
6	540	30 35	2.67	0.375
7	567	38 47	2.42	0.413
9	591	49 0	1.98	0.505
9	532	55 47	1.75	0.571
6	314	63 11	1.55	0.645
6	331	68 47	1.64	0.610
8	364	82 8	1.35	0.741
6	246	89 15	1.22	0.820

It was found that the reciprocal of the number of particles per c.c. plotted against time gave a straight line in every case within the limits of experimental error*; that is, the rate of coagulation of the clouds followed the law

$$\frac{1}{n} = \frac{1}{n_0} + Kt, \quad . \quad . \quad . \quad . \quad (4)$$

where n is the number of particles per c.c. at time t , and n_0 is the initial number of particles.

It is therefore possible to tabulate the values for the initial number of particles per c.c., obtained by extrapolation, and the values for the coagulation constant as the

* This result has also been arrived at independently by H. S. Patterson, and the nomenclature suggested by him has been adopted

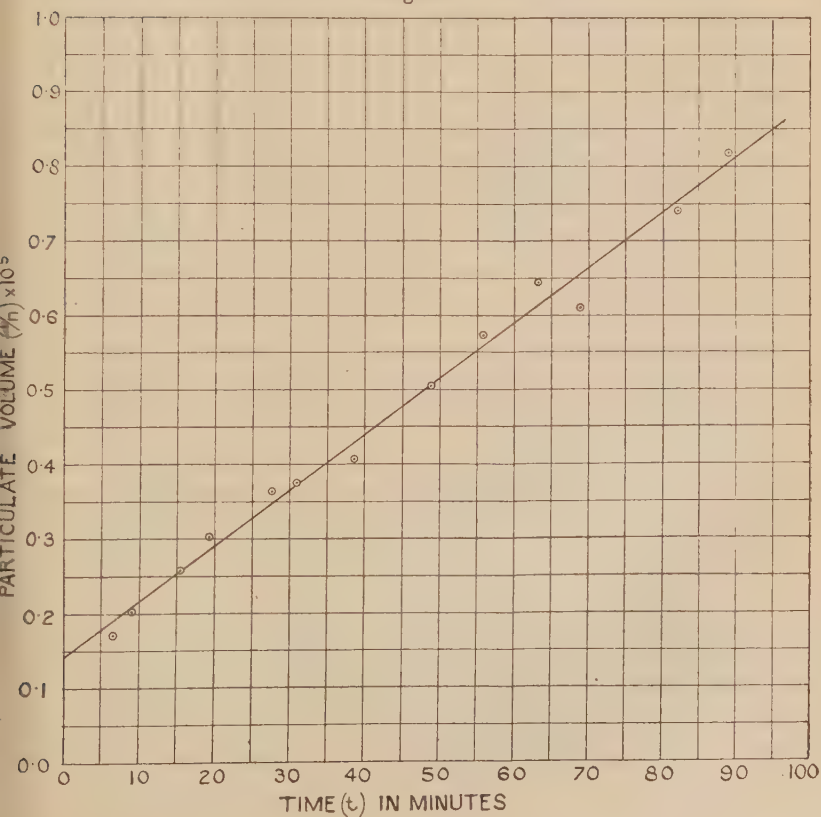
factor K will be termed, for a number of clouds thus :—

TABLE III.

Concentration (mg. per c. metre). c .	Initial number of particles per c.c. $n_0 \times 10^{-5}$.	K. $\text{cm.}^3/\text{min.} \times 10^3$.
2.0	6.94	7.42
4.0	6.25	7.85
5.8	6.45	7.45
6.5	8.00	6.40
6.8	8.70	5.00
*15.0	9.35	5.12
*15.0	6.78	4.74
*15.0	6.67	4.20
18.6	8.70	3.90
23.6	9.44	4.70

* These clouds were generated from an open heater—nichrome ribbon wound on mica, heated electrically.

Fig. 3.



The values of K show a decrease as the concentration, *i. e.* initial size of particle, increases.

Although the conditions of generation of the clouds were kept constant as far as possible, the number of particles which may be formed initially for any given concentration may vary within rather wide limits, *e. g.* three clouds of 15 mg. concentration contained 9.35×10^5 , 6.78×10^5 , and 6.67×10^5 particles per c.c. respectively. It seems that small differences in the way the vapour coming off the boat condenses and is subsequently diluted by fanning may make a considerable difference in the number of particles initially formed, and, unless more precise methods of producing these clouds are adopted, more closely reproducible results are not likely to be obtained.

However, it is noteworthy that the initial numbers on the whole increase slowly with concentration, and considering that the concentration varied by ten-fold this increase is somewhat surprisingly small.

A hypothesis which provides an explanation for this result is that the degree of dispersion of a cloud formed from vapour depends upon the degree of supersaturation of the vapour and the number and size of nuclei present in the air.

The vapour pressure of ammonium chloride is very low at normal temperatures so that a high degree of supersaturation probably existed over the heated boat. Now the degree of supersaturation would be more or less the same in all the experiments since only the time of dispersal was altered and the other conditions were kept constant as far as possible. Further, the air probably contained a fairly constant number of nuclei, since it had been rendered dust-free by passage through a filter.

Possibly both these nuclei and single or complex molecules of ammonium chloride act as condensation centres for the vapour as it first comes off the boat, and the particles so formed are drawn over the boat time and time again with the net result that their size is increased and very few fresh nuclei are brought into play as the dispersal is continued: hence the number of particles formed initially would increase very slowly with the concentration.

It is doubtful whether the air itself contained sufficient nuclei to act as centres of condensation for the formation of all the particles. Wilson* showed that there is a large number of nuclei present even in dust-free air, and estimated

* C. T. R. Wilson, *Phil. Trans. A*, cxcix. p. 265 (1897).

their number as being of the order 10^8 per c.c. Andrén *, however, dealing with air which had been carefully purified by previous cooling to -78° C., obtained a maximum figure of 10^4 per c.c. when the air was saturated with water-vapour. These nuclei were considered by him to be complex water molecules. He also concluded that Wilson's estimate was too high.

An attempt has therefore been made to estimate the number of nuclei in air, freed from dust particles and then saturated with water-vapour. A small plunger type of Wilson apparatus, similar to the one described in the first part of this paper but having an ultra-microscope cell 3 cm. in diameter, was set up and the number of nuclei revealed at various expansion ratios determined by the photographic method.

A wider cell was made since it was doubtful whether the original narrow cell would have given a truly adiabatic expansion when the ratio was increased to a high limit, but the photographic arrangements were the same as those employed with the continuous-action Wilson apparatus. One difficulty encountered was due to the droplets moving very rapidly downward with a velocity greater than their terminal velocity immediately after their formation, when the expansion ratio was high, *i. e.* the cooling was very great. The intensity of the light was not sufficient to allow exposures of less than $1/50$ th second to be made, so that it was necessary to wait until the droplets slowed up before taking a photograph, and a few may have been lost owing to evaporation. The following results were obtained:—

TABLE IV.

Expansion ratio.	Degree of Supersaturation.	No. of nuclei per c.c. $\times 10^{-14}$.	No. of nuclei per c.c. $\times 10^{-14}$ (Andrén).
1.330	6.50	0.56	0.10
1.375	8.05	2.24	0.70
1.416	9.67	4.45	4.00
1.468	12.15	5.32	10.00 ca.
1.570	18.18	9.95	10.50 ca.

These results are in fair agreement with those of Andrén,

* Andrén, *Ann. d. Physik*, lii. p. 1 (1917).

although there is no indication of a "saturation" value being reached, a discrepancy that may be due to differences in the experimental conditions.

However, they serve to give an estimate of the number of nuclei in moist dust-free air which may act as centres of condensation for the formation of the ammonium chloride particles.

Results for Cadmium Oxide Clouds.

It was necessary to shorten the connecting tube between the Wilson apparatus and the chamber to 10 cm., since owing to the greater density of cadmium oxide there were considerable losses of particles in the long connecting tube. Clouds were formed by arcing between cadmium electrodes for 45 seconds, a current of 3 amperes being employed.

The clouds showed similar behaviour to the ammonium chloride ones. Results have been tabulated in the same way as before and a typical particulate volume curve has been plotted in fig. 4.

TABLE V.

Cloud.	Initial number of particles per c.c. $n_0 \times 10^{-6}$.	K. $\text{cm.}^3/\text{min.} \times 10^3$.
I.	1.25	5.28
II.	1.08	4.65
III.	0.94	4.36
IV.	0.95	4.84
V.	1.37	3.84

Comparison between the Results Obtained by applying the Aitken Effect and those by using the Ultra-microscope directly.

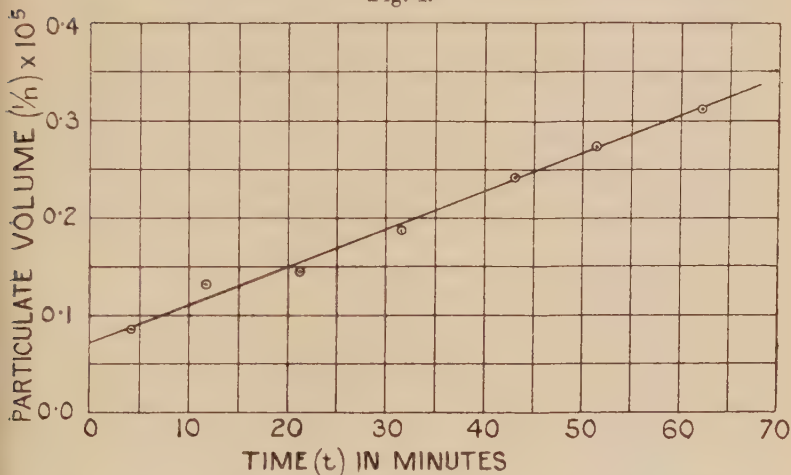
The writer has had the opportunity of comparing his results with recent ones obtained with a new type of visual ultra-microscope by Whytlaw-Gray. In this instrument the defects of the original type have been completely eliminated.

The limit of size of particle which can be detected visually is of the order 1×10^{-6} cm. radius, whilst the continuous-action Wilson apparatus would detect particles even smaller than 1×10^{-7} cm. in radius. A comparison

between the respective sets of results, particularly in regard to the slopes of the particulate volume curves, leads to the definite conclusion that the number of amicroscopic particles in these clouds is negligibly small.

In the case of cadmium oxide there do not appear to be any free ions of very small dimensions after the first few minutes; any such ions that are produced by the arc must be picked up by the visible particles within a very short space of time. No counts were made before three minutes

Fig. 4.



after dispersal of the clouds; there is a certain indication that the observations with the Wilson apparatus at this time are rather on the high side, and this may be due to the existence of free ions of a very small size.

Application of Smoluchowski's Theory.

The constant K has a wider significance if the coagulation of these clouds be considered from the point of view of Smoluchowski's theory of the mechanism of coagulation of sols. Smoluchowski*, by mathematical treatment of the chance collisions of particles owing to diffusion, derived an equation which can be expressed in the form

$$\frac{1}{n} = \frac{1}{n_0} + Kt, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $K = 4\pi D \cdot Ra$, D being the diffusion coefficient and Ra the radius of sphere of action of a particle of radius r .

* Smoluchowski, *Zeit. f. Physik. Chem.* xcii. p. 129 (1918).

Whytlaw-Gray has calculated the value of K by substituting known values for the physical constants involved; putting in the constants for the conditions under which the clouds in these experiments were formed, it is found that

$$K = 8.63 \times 10^{-9} \frac{(1 + 9 \times 10^{-6})}{r} \frac{Ra^{1/2}}{r} \text{ cm.}^3/\text{min.}$$

Owing to the

fact that it is necessary to apply the Cunningham correction to the term for the mobility of the particles involved in the diffusion constant, K is no longer a constant but becomes a function of the radius of the particle. Assuming that the radius of sphere of action of a particle is twice its radius, it is possible to calculate the value for K for each of the ammonium chloride clouds in its initial stages. It is further necessary to assume an average value for the initial radii of the particles calculated from the weight of substance dispersed, the number of particles per c.c., and a density of the substance, taken as being that of the substance in bulk.

The figures for the series of clouds are tabulated below:—

TABLE VI.

Initial Average Radius of Particles. cm. $\times 10^5$.	K found. cm. ³ /min. $\times 10^8$.	K calculated. cm. ³ /min. $\times 10^8$.	K found/ K calculated.
0.75	7.42	3.78	1.96
1.02	7.85	3.26	2.41
1.07	5.00	3.18	1.65
1.08	6.40	3.17	1.93
1.12	7.45	3.12	2.38
1.36	5.12	2.88	1.84
1.49	3.90	2.77	1.41
1.52	4.74	2.76	1.72
1.53	4.20	2.76	1.52
1.56	4.70	2.73	1.74

No figures have been calculated for the cadmium oxide clouds since the concentrations were unknown.

The discrepancies between the actual and theoretical values of K for ammonium chloride are not any greater than might be expected, since the theoretical values were calculated on the simplest possible assumptions. There are several directions in which divergencies between the theoretical and practical conditions may arise.

(a) It has been assumed in making the calculations that the particles in the clouds are solid uncharged spheres and that coalescence takes place purely owing to particles coming into chance collision through diffusion. But it has been established by Patterson and Whytlaw-Gray* that particles are not necessarily spherical and that aggregates have a loose structure. The term "radius of sphere of action" cannot therefore have an exact significance, and its value may be several times that calculated on the basis that the original particles and complex particles are compact spheres.

(b) Although the majority of particles were uncharged when the clouds were generated, they picked up charges as the cloud aged owing to the natural ionization of the air. It is possible that the charges on particles exert some influence on the rate of coagulation of the cloud.

(c) No allowance has been made in these calculations for losses of particles due to falling out or diffusion to the sides of the chamber, but Whytlaw-Gray has shown that these would be small during the first hour and a half of the history of clouds of this type. Any such losses would tend to increase the apparent value of K .

(d) The density of the particles and of complexes in particular is likely to be less than that of the substance in bulk †, and therefore on this account the calculated values of K are possibly too high.

(e) All collisions have been considered effective in producing coalescence of particles, but if only a proportion are effective the theoretical values of K have again been over-estimated.

Until the influence of these factors has been investigated in detail it will not be possible to state definitely to what extent the Smoluchowski theory holds when applied to aerosols.

In conclusion, I should like to express my indebtedness to Professor R. Whytlaw-Gray, whose pioneer work on smokes was the inspiration of this research, and to Mr. J. D. Fry for their kind advice and criticism.

* H. S. Patterson and R. Whytlaw-Gray, Proc. Roy. Soc. A, cxiii. p. 302 (1926).

† H. S. Patterson and R. Whytlaw-Gray, *loc. cit.*

XCVII. *Atomic Structure and the Magnetic Properties of Coordination Compounds.*—Part II. By L. C. JACKSON, M.Sc., Ph.D., A.Inst.P., Henry Herbert Wills Research Fellow, Department of Physics, The University, Bristol*.

IT is proposed in the present paper to continue further the discussion of the magnetic properties of coordination compounds in the light of the schemes put forward by Welo and Baudisch, by Bose, and by Cabrera†. Special reference will be made to those compounds the properties of which appear to be anomalous and to present difficulties to the explanatory schemes suggested. In addition the discussion, which was confined in Part I. to the case of mononuclear coordination compounds, is extended to the case of those multinuclear compounds the magnetic properties of which are known.

Anomalies and Difficulties.

The theories discussed in Part I. set out to provide an explanation in terms of electronic distributions of the magnetic properties of coordination compounds, taking these properties to be such that compounds of Co^{+++} , Fe^{++} are diamagnetic, and those of Cr^{+++} , Fe^{+++} , Ni^{++} , Cu^{++} are paramagnetic with Weiss magneton numbers approximately equal to 19, 11, 16, and 10 respectively, except for the carbonyls, which received separate treatment. The majority of sixfold and fourfold coordination compounds which have been investigated actually possess the magnetic properties enumerated above, but there are various exceptions which do not fit directly into the scheme put forward. It is proposed to discuss these anomalies now.

In the first place, we may mention the iron and nickel carbonyls, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$. The theories of Welo and Baudisch and of Bose can give apparently satisfactory explanations of the magnetic properties of these compounds, both of which are diamagnetic. They were not, however, discussed in Part I., as the paper was limited to the material which is common to the three papers considered, and Cabrera does not deal with these compounds. It may be pointed out here that Cabrera's scheme is, however, able to give an explanation of the magnetic properties of the iron and nickel carbonyls in a manner not more arbitrary than the other

* Communicated by the Author.

† For a list of references see Part I. of this paper, *Phil. Mag.* ii. 86 (1926).

two schemes. If the two compounds are formulated as $[\text{Ni}(\text{CO})_3]\text{CO}$ and $[\text{Fe}(\text{CO})_4]\text{CO}$, and the two metals being divalent and each CO group involving the transfer of two electrons as assumed by Welo and Baudisch and by Bose, the Fowler scheme for the distribution of the "binding electrons" will hold. Then the iron carbonyl will be expected to be diamagnetic, as are other coordination compounds of ferrous iron, the electron distribution in the Fe^{++} ion being the same in the two cases. On the other hand, the nickel carbonyl, if supposed to have the same electron distribution in the Ni^{++} ion as in other nickel coordination compounds, would be expected to be paramagnetic. If, however, in this compound the electron distribution is

$$\begin{array}{ccc} M_{32} & M_{33} & N_{11} \\ 0 & 6 & 2 \end{array}$$

in place of that assumed for other (in Cabrera's scheme only for sixfold) compounds of nickel, viz.

$$\begin{array}{ccc} M_{32} & M_{33} & N_{11}, \\ 2 & 6 & 0 \end{array}$$

then the carbonyl would be diamagnetic, as is observed. This assumption may seem arbitrary, but something of the kind is necessary, as there are also nickel coordination compounds such as $\text{Na}_2\text{Ni}(\text{CN})_4$ which are diamagnetic and which present a difficulty to the three theories discussed in Part I. The case of these compounds will be discussed in a later section.

It may be mentioned that Bose states that in his scheme the coordination number appears as half the difference in the number of electrons in the normal ion and that in the coordinated atom. If, as it would appear, he takes the nickel and iron carbonyls as being fourfold and fivefold compounds respectively, then he must attribute the valency zero to the normal ion. This point is similar to the definite suggestion recently put forward by Weiss* that the metallic atom in these carbonyls has a valency zero; but this does not seem likely to be generally acceptable.

The next example of an apparently anomalous substance may be ferric acetylacetonate, the properties of which have been determined by Feytis† and Ishiware‡. In this case the magnetic moment corresponds to that in simple salts. It would then seem that the coordinated atoms in these

* *Comptes Rendus*, clxxxiv. p. 417 (1927).

† *Comptes Rendus*, clii. p. 708 (1911).

‡ *Sci. Rep. Tohoku*, iii. p. 303 (1914).

compounds have the same electronic distribution as in the ions of the corresponding simple salts. This requirement would raise a considerable difficulty for the theories of Welo and Baudisch and of Bose, in which the electrons from the coordinating groups pass into the structure of the central atom. It does not, however, present any such difficulty for Cabrera's scheme.

If each acetylacetone group gave up only one electron, then the compound could theoretically be formulated as threefold in a manner consistent with the Fowler scheme and with the magnetic properties. However, each acetylacetone group is regarded chemically as linked to the ferric ion by a principal and a subsidiary valency, and it does not seem satisfactory that these two bonds should be represented by the transference of a single electron. On the other hand, if each group gives up three electrons, the compound can be formulated as sixfold in the same way as $[\text{Co}(\text{en})_3]\text{Cl}_3$ is regarded as sixfold. The compound would then be expected to be paramagnetic with a magneton number of approximately 11. One might, however, reject the idea that the symmetry of the arrangement of the outer groups and their "binding electrons" is responsible for the rearrangement among the electrons of the M level of the central atom. If this is done then there will be no obvious reason why the electronic arrangement should not in some cases be the same as in simple salts. Cabrera's scheme, with the limitation mentioned, would thus be able to include also coordination compounds whose magnetic properties are those of simple salts rather than those associated with the majority of such compounds. It would then be proposed to accept the general scheme proposed by Cabrera; but there would still have to be found some more general reason for the distribution of the electrons than that originally suggested. On the other hand, one may not have to reject any part of Cabrera's scheme, for it may be that in ferric acetylacetonate, a compound of quite different class from the sixfold compounds such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ with which Cabrera deals, the actual symmetry of the distribution of the "binding electrons" may be quite different from that in the other class of compounds mentioned. The tendency to redistribute the electrons of the M level of the Fe^{+++} ion would then be absent, so that ferric acetylacetonate would be expected to have the same magnetic properties as simple ferric salts.

Further examples of coordination compounds with magnetic properties differing from those usually found can be mentioned. Thus the complex nickel cyanides

$\text{Na}_2\text{Ni}(\text{CN})_4$ and $\text{K}_2\text{Ni}(\text{CN})_4$ are stated by Depold* to be diamagnetic. No immediate explanation of this anomaly seems to be possible on the schemes of Welo and Baudisch and of Bose, but, by applying to these compounds the idea previously mentioned when dealing with the carbonyls, a generalization of the scheme proposed by Cabrera does seem capable of furnishing an explanation.

One other point may be mentioned while dealing with difficulties encountered by the theories. At the end of Part I. it was mentioned that while generally compounds such as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ would be regarded magnetically as examples of simple salts, they have been formulated by Werner as typical sixfold coordination compounds $[\text{Co}(\text{OH}_2)_6]\text{Cl}_2$ and $[\text{Ni}(\text{OH}_2)_6]\text{SO}_4$. It would seem necessary to consider whether there is any evidence from the magnetic data to enable one to distinguish between the two viewpoints and, in particular, to show that the latter is not in contradiction with the observed properties. It may be stated immediately that the magnetic data cannot decide the question, as we have seen that typical coordination compounds may either always have the same properties as the simple salts as in Cr^{+++} or may exceptionally possess them rather than those usually attributed to coordination compounds as in Fe^{+++} . To take, however, the particular examples cited above, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, it would be expected with a large degree of certainty that $[\text{Ni}(\text{OH}_2)_6]\text{SO}_4$ would be paramagnetic with a magneton number of approximately 16, as is actually the case. One cannot say with equal certainty what would be the magnetic properties of $[\text{Co}(\text{OH}_2)_6]\text{Cl}_2$ as we have no data for sixfold coordination compounds of divalent cobalt. In all the coordination compounds of cobalt investigated by Rosenbohm this element was trivalent. In cobaltous acetylacetonate,

$\text{Co}\left(\frac{\text{CH}_3\text{CO}}{\text{CH}_3\text{CO}}\right)_2\text{CH}$, we have, however, an example of a coordination compound of divalent cobalt. The susceptibility of this substance at atmospheric temperature has been determined by Feytis†. From the value given, it is seen that the assumption of a reasonable value for Δ would make the magneton number equal to that found in the simple salts of divalent cobalt. Thus, as far as the evidence goes, it seems probable that the majority of coordination compounds of divalent cobalt would have the same magnetic properties

* Dissertation, Halle (1913).

† *Comptes Rendus*, clii. p. 708 (1911).

as the simple salts, just as is the case with the corresponding salts of divalent nickel. It would therefore be expected that $[\text{Co}(\text{OH}_2)_6]\text{Cl}_2$ would be paramagnetic with a magneton number of approximately 24. The formulation of the hexahydrates as sixfold coordination compounds, at least in the cases considered, would then not be in disaccord with the observed magnetic properties.

Possible Experimental Test of the Theories.

It would seem to be just within the limits of possibility to make an experimental test of the various schemes that have been proposed for the explanation of the magnetic properties of coordination compounds. According to the schemes of Welo and Baudisch and of Bose, the number of electrons associated with the central coordinated atom is considerably greater than that of the normal ion in simple salts. In Cabrera's scheme the number of electrons associated with the central atom is the same as in the simple salts, the "binding electrons" forming a group associated with the molecule as a whole. It would therefore seem possible that a study of the intensity of the reflexion of X-rays from crystals of coordination compounds and simple salts of the same element would serve to determine whether the larger electron concentration in the central atom in the coordination compounds as postulated by the first two theories is actually present. On Cabrera's scheme the scattering power of the metallic atom should be very approximately the same in the two classes of compound, the change in scattering power due to the rearrangement of the electrons in the M level being probably too small to be detected experimentally. The proposed investigation would therefore seem able to serve as a definite test of the theories.

The Magnetic Properties of Multinuclear Coordination Compounds.

Of the data available concerning the magnetic properties of multinuclear coordination compounds, the majority are due to Rosenbohm. In addition, a few compounds have been measured by Feytis. The information given in Rosenbohm's paper relates only to compounds of cobalt and of chromium, and the measurements were carried out only at atmospheric temperature, so that the data available for discussion are as yet meagre and the magnetic moments of the molecules are uncertain.

BINUCLEAR COMPOUNDS I.

Rosenbohm gives the values of the susceptibilities of a large number of "position" isomers of the type $[\text{Cr}(\text{NH}_3)_6]$ $[\text{Co}(\text{ON})_6]$, $[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{CN})_6]$. The data are reproduced below in Table I.

TABLE I.

Substance.	$\chi \times 10^6$.	$\chi_{\text{corr.}} \times 10^6$.	$M_{\text{corr.}} \times 10^6$.
$[\text{Cr}(\text{NH}_3)_6]$ $[\text{Co}(\text{ON})_6]$	17.78	17.05	6287
$[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{CN})_6]$	17.99	17.25	6364
$[\text{Cr}(\text{en})_3]$ $[\text{Cr}(\text{CN})_6]$	31.60	30.29	13340
$[\text{Cr}(\text{en})_3]$ $[\text{Co}(\text{CN})_6]$	14.64	14.04	6277
$[\text{Co}(\text{en})_3]$ $[\text{Cr}(\text{CN})_6]$	14.81	14.19	6364
$[\text{Cr}(\text{pn})_3]$ $[\text{Cr}(\text{CN})_6]$	28.67	27.48	13270
$[\text{Cr}(\text{pn})_3]$ $[\text{Co}(\text{CN})_6]$	13.43	12.87	6287
$[\text{Co}(\text{pn})_3]$ $[\text{Cr}(\text{CN})_6]$	13.61	13.05	6374
$[\text{Co}(\text{pn})_3]$ $[\text{Co}(\text{CN})_6]$	-0.332	-0.318	-154
$[\text{Cr}(\text{NH}_3)_6]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$	29.57	28.34	13320
$\left[\begin{smallmatrix} (\text{NH}_3)_4 \\ \text{Cr} \\ (\text{C}_2\text{O}_4) \end{smallmatrix} \right]$ $\left[\begin{smallmatrix} (\text{NH}_3)_2 \\ \text{Cr} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$	29.56	28.33	13320
$[\text{Cr}(\text{NH}_3)_6]$ $[\text{Co}(\text{C}_2\text{O}_4)_3]$	18.80	18.01	8597
$[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$	13.75	13.18	8597
$[\text{Cr}(\text{en})_3]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$	25.41	24.35	13360
$\left[\begin{smallmatrix} (\text{en})_2 \\ \text{Cr} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$ $\left[\begin{smallmatrix} (\text{en}) \\ \text{Cr} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$	25.39	24.33	13330
$[\text{Cr}(\text{en})_3]$ $[\text{Co}(\text{C}_2\text{O}_4)_3]$	14.41	13.81	7640
$\left[\begin{smallmatrix} (\text{en})_2 \\ \text{Co} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$ $\left[\begin{smallmatrix} (\text{en}) \\ \text{Cr} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$	12.02	11.52	6384
$[\text{Co}(\text{en})_3]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$	12.00	11.50	6374
$\left[\begin{smallmatrix} (\text{en})_2 \\ \text{Cr} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$ $\left[\begin{smallmatrix} (\text{en}) \\ \text{Co} \\ (\text{C}_2\text{O}_4)_2 \end{smallmatrix} \right]$	12.17	11.66	6509
$[\text{Cr}(\text{pn})_3]$ $[\text{Co}(\text{C}_2\text{O}_4)_3]$	11.74	11.25	6727
$[\text{Co}(\text{pn})_3]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$	10.93	10.48	6287
$[\text{Cr}(\text{en})_3]$ $[\text{Cr}(\text{SCN})_6]$	21.97	21.06	13320
$[\text{Cr}(\text{pn})_3]$ $[\text{Cr}(\text{SCN})_6]$	20.63	19.77	13350
$\left[\begin{smallmatrix} (\text{en})_2 \\ \text{Cr} \\ (\text{SCN})_2 \end{smallmatrix} \right]_3$ $[\text{Cr}(\text{SCN})_6]$ cis.	22.00	21.09	26720
	trans. 22.03	21.11	26760

In the above table the second column gives the values of

the susceptibilities direct from Rosenbohm's paper, the third and fourth columns the susceptibilities and molecular susceptibilities respectively corrected as mentioned below; *en* and *pn* stand for ethylenediammine and propylenediammine respectively.

Firstly, it may be pointed out that, formally at least, the ideas put forward by Fowler concerning the structure of mononuclear coordination compounds will apply also to these binuclear compounds. Taking both cobalt and chromium to be tervalent in these substances and calculating the number of electrons shared with or transferred to the coordinated atoms, we find that the total is always twenty-four.

On examining Table I. it will be seen that, as in the majority of other coordination compounds, those containing Co^{+++} are diamagnetic and those containing Cr^{+++} are paramagnetic. As will be seen later, the magnetic moment possessed by the chromium atom is the same approximately as that in the mononuclear compounds, and hence the electronic arrangements in the Co^{+++} and Cr^{+++} ions are respectively the same in the two classes of compounds, so that the points under discussion in Part I. will apply equally.

The corrected values in columns 3 and 4 of Table I. have been recalculated from Rosenbohm's data, using the now accepted value for the susceptibility of water 0.719×10^{-6} instead of 0.75×10^{-6} as used by Rosenbohm. On examining the last column of Table I. certain regularities pointed out by Rosenbohm will be apparent, constant differences in susceptibility occurring in pairs of "position" isomers, the values about 6287 and 6364 reappearing several times. Certain substances in the table, oxalate-compounds, appear to be anomalous, the molecular susceptibilities being considerably greater than in the other compounds in the list. This anomaly is in each case apparently due to the presence of the group $[\text{Co}(\text{C}_2\text{O}_4)_3]$. It must be mentioned that Feytis has also investigated some of the substances in question and did not obtain abnormally high values, but her values for the susceptibilities even of other compounds are consistently lower than those of Rosenbohm. The compounds are worthy of further study with a view to clearing up the present discrepancy in the information.

To obtain some idea of the magnitude of the magnetic moment carried by the chromium atoms in these binuclear compounds and of the probable order of accuracy of the data, the Weiss magneton numbers have been calculated for several of the compounds and are given in Table II. It is, however, to be emphasized that nothing is known of the

temperature variation of the susceptibilities of the compounds, and the supposition that they all obey Curie's law is a pure assumption. A study of the thermal variation is necessary before an adequate discussion of the data can be made. Before one can calculate the magneton number of the chromium atom, one must be able to evaluate the correction to be applied to the molecular susceptibilities to allow for the contributions due to the other parts of the molecule. Thus in the compound $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ the diamagnetism of the NH_3 and CN groups can be allowed for, using Pascal's data; but one has also to bear in mind that the cobalt atom in such compounds carries a small but definite positive moment of as yet unknown origin. It is more convenient to treat the groups $[\text{Co}(\text{NH}_3)_6]$, $[\text{Co}(\text{CN})_6]$, etc., as a whole. Their properties can be deduced from Rosenbohm's data as follows. The molecular susceptibility of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is known, and the contribution of the Cl_3 is obtained from Pascal's data; hence the part of the molecular susceptibility due to the $[\text{Co}(\text{NH}_3)_6]$ group can be calculated. The same process can be applied to $[\text{Co}(\text{en})_3]$ and $[\text{Co}(\text{pn})_3]$. That of $[\text{Co}(\text{CN})_6]$ cannot be obtained in the same way, but the molecular susceptibility of $[\text{Co}(\text{pn})_3][\text{Co}(\text{ON})_6]$ is given in Table I., and the required value can be obtained from this.

The corrected values of the molecular susceptibilities of such of the mixed chromium-cobalt compounds as can be treated in this way, and also of the compounds containing only chromium in which the diamagnetic proportion of the NH_3 , CN , etc., groups has also been allowed for, are given in Table II.

Table II.

Substance.	$M' \times 10^6$	n .
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	6690	
$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$	6770	
$[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$	6737	19.3
$[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$	6833	(From mean of previous column.)
$[\text{Cr}(\text{pn})_3][\text{Co}(\text{CN})_6]$	6780	
$[\text{Co}(\text{pn})_3][\text{Cr}(\text{CN})_6]$	6870	
$[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6]$	14139	19.7
$[\text{Cr}^{(\text{en})_2}_{(\text{SCN})_2}][\text{Cr}(\text{CN})_6]$	28505	20.1

The values now do not show the regularities noticed in column 3 of Table I. The Weiss magneton numbers are

given in column 3 of Table II. They appear to increase with increasing molecular weight of the compound. This is possibly only apparent, and may be due to these substances not following Curie's law. The magneton numbers are, however, all of the same order of magnitude as those found in the mononuclear coordination compounds and in the simple salts of trivalent chromium, so that these compounds do not seem to show any new features of interest.

BINUCLEAR COMPOUNDS II.

A further class of compounds containing two coordinated atoms have been investigated by Rosenbohm. These are the diol compounds contained in Table III. All the values of the susceptibilities have been corrected to 0.719×10^{-6} for the susceptibility of water.

TABLE III.

Substance.	$\chi \times 10^6$.	$M \times 10^6$.	$M' \times 10^6$	n .
$\left[\begin{array}{cc} \text{OH} & \\ (\text{NH}_3)_4\text{Co} & \text{Co}(\text{NH}_3)_4 \\ \text{OH} & \end{array} \right] \text{Cl}_4 + 4\text{H}_2\text{O}$	-2.14			
" $\text{Br}_4 + 4\text{H}_2\text{O}$	-1.14			
" $(\text{SCN})_4$	-1.03			
$\left[\begin{array}{cc} \text{OH} & \\ (\text{en})_2\text{Co} & \text{Co}(\text{en})_2 \\ \text{OH} & \end{array} \right] \text{Br}_4 + 2\text{H}_2\text{O}$	-1.85			
" $(\text{NO}_2)_4$	-2.53			
$\left[\begin{array}{cc} \text{OH} & \\ (\text{en})_2\text{Cr} & \text{Cr}(\text{en})_2 \\ \text{OH} & \end{array} \right] \text{Br}_4$	14.66	10225	10545	17.4
" I_4	12.36	10948	11335	18.0
$\left[\begin{array}{cc} \text{OH} & \\ (\text{C}_2\text{O}_4)_2\text{Cr} & \text{Cr}(\text{C}_2\text{O}_4)_2 \\ \text{OH} & \end{array} \right] \text{Na}_4$	14.81	8620	8799	15.9

The cobalt compounds are diamagnetic and the chromium compounds paramagnetic, as was to be expected. The agreement among the values of the magneton numbers of the chromium compounds is not at all good, but may be due to the substances showing different deviations from Curie's law. The values for the first two compounds are, allowing a reasonable Δ in each case, sufficiently near to the value

found for simple salts and the mononuclear compounds to suggest that the chromium atoms possess the same electronic configuration in all the compounds.

TRINUCLEAR COMPOUNDS.

Rosenbohm gives the values of the susceptibilities of the chromium coordination compounds containing three chromium atoms, the formulæ of which are as follows :—

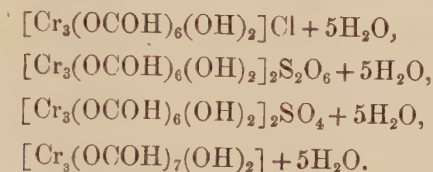


TABLE IV.

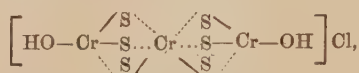
Substance.	$\chi \times 10^6$.	$M \times 10^6$.	$M' \times 10^6$.	n .
$[\text{Cr}_3(\text{OCOH})_7(\text{OH})_2] + 5\text{H}_2\text{O}$	23.76	14137	14344	16.6
$[\text{Cr}_3(\text{OCOH})_6(\text{OH})_2]\text{Cl} + 5\text{H}_2\text{O}$	24.83	14540	14748	16.8
$[\text{Cr}_3(\text{OCOH})_6(\text{OH})_2]_2\text{S}_2\text{O}_6 + 5\text{H}_2\text{O}$	23.51	27510	27885	16.3
$[\text{Cr}_3(\text{OCOH})_6(\text{OH})_2]_2\text{SO}_4 + 5\text{H}_2\text{O}$	22.51	24890	25240	15.5

Rosenbohm's values have been corrected as before. The first three chromium compounds, on assuming Curie's law, give Weiss magneton numbers approximating to 16.5. (The fourth compound as it stands appears to be anomalous, giving 15.5. If, however, the figures 23.48 in the original paper were a misprint for 25.48, the compound would fall into line with the others.)

The absence of any knowledge of the actual temperature variation of the susceptibilities of these compounds prevents anything definite being stated with regard to the configuration of the paramagnetic atoms, but the value 16.5 for the chromic compounds suggests an idea which may not be too speculative to be mentioned here.

These magneton numbers are considerably different from those met with in other coordination compounds. This suggests that the three atoms in the molecule do not all carry the same magnetic moment so that the calculated magneton numbers are "effective" magneton numbers obtained by taking the root-mean-square of the values

actually present. From a consideration of the configurations of the molecules, the formula of the dihydroxyhexaformato-chromi chloride being written



in which S stands for the formato group O·COH and full lines for principal valencies and dotted lines for subsidiary valencies, it seems not unlikely that the central chromium atom may be in a different state from the other two. If, now, it is assumed that there really exists a small negative Δ for all these compounds so that the actual magneton numbers are somewhat smaller than those calculated on the assumption of Curie's law, then the values obtained will be reproduced if the chromium atoms carry moments equal to 19, 0, 19 Weiss magnetons. The value usually found for chromium compounds is 19. This can easily be verified by a simple calculation; but the actual values are not given here, since there can be no question at present of any accurate numerical agreement between the observed and calculated values.

Summary.

The discussion of the magnetic properties of coordination compounds is continued in the light of the theories of Welo and Baudisch, of Bose, and of Cabrera. Particular attention is paid to those compounds which are apparently anomalous and which present various difficulties to the theories as yet proposed. The conclusion is reached that Cabrera's scheme is better able to account for the magnetic properties of coordination compounds in general than the other two schemes.

The discussion which was limited in Part I. of the present paper to the mononuclear coordination compounds is now extended to the multinuclear coordination compounds.

The H. H. Wills Physical Laboratories,
The University, Bristol.
May 1927.

XCVIII. *Resonant Circuits with Reactive Coupling.*

By R. T. BEATTY, *M.A., B.E., D.Sc.**

1. *Introduction.*

IN this paper the fundamental equations considered are linear with constant coefficients, so that the discussion must be limited to the subject of amplification over a linear region of the characteristic curve and under conditions where the grid current is negligible: that is, the amplification is without distortion. The problem is simplified without using approximations by the introduction of equivalent circuits, and a representation by means of curves derived from a parabola is given, by help of which the behaviour of the circuits can be ascertained by inspection.

The geometry of the parabola is used to facilitate the discussion of amplification and resonance curves, and an attempt is made to give a quantitative basis for the treatment of selectivity by the introduction of two new terms—"tolerance" and "activity."

LIST OF SYMBOLS.

General Circuits.

Z_0	a_0	impedance, admittance of	grid-plate	circuit.	
Z_1	a_1		plate		
Z_2	a_2		grid		
i_0	i_1	i_2	alternating currents flowing through Z_0 Z_1 Z_2 .		
e	alternating e.m.f. injected in grid circuit.				
e_1	alternating p.d. between	plate and filament	grid and filament		
e_2					
S	internal	resistance	from plate to filament.		
s_X		admittance			
a_{g1}	equivalent	total	grid input admittance.		
a_g					
$g = \mu s_X$	mutual conductance of valve.				
K_0	s_0	capacity, inductance, conductance of	grid-plate	circuit.	
K_1	L_1		plate		
K_2	L_2		grid		

* Communicated by the Author.

Equivalent Circuits.

$C_0 - \sigma_0$	capacity, inductance, conductance of	grid-plate	circuit.
$C_1 L_1 \sigma_1$		plate	
$C_2 L_2 \sigma_2$		grid	
$\omega_1 \omega_2$	pulsatance at resonance	of plate circuit	of grid circuit.
$m_1 m_2$	maximum voltage		
	amplification		
* $\alpha_1 \alpha_2$	log of ratio of impressed pulsatance to that		
$t_1 t_2$	tangent of phase-angle		
$\sinh \alpha_1 = \partial \omega / \omega_1$	} approximately.		
$\sinh \alpha_2 = \partial \omega / \omega_2$			
g	mutual conductance of equivalent valve.		
ω	pulsatance of impressed frequency.		
ω_0	pulsatance to which whole circuit is tuned.		
m	m_1 or m_2 when $m_1 = m_2$.		
$p = C_0 \omega / g$.			
$N_1 = \sigma_0 g / \sigma_1 \sigma_2$.			
$N_2 = C_0 \omega g / \sigma_1 \sigma_2$.			
$N / \nu = N_1 + j N_2$.			
T	tolerance	of circuit or circuits: values in Table.	
Ac	activity		
$\partial \omega / \omega_0$	frequency departure		
y	ordinate of resonance curve.		
$A = C_2 \omega_2 g / \sigma_1 \sigma_2$	{ maximum voltage amplification for two circuits without reaction.		
F_0	reaction factor.		
F / ϕ	vector whose maximum modulus is F_0 .		
$t_0 = \tan \theta_0$	value of $t_1 = t_2$ corresponding to F_0 .		
h	$= m_1 / m_2$.		
β	$= 4h / (1 + h)^2$.		

Geometrical.

xy	coordinates of origin of vector N .		
$x_h y_h$	coordinates of a point corresponding to h .		
l		length of any line,	to parabola from xy
l_h		length of normal	to parabola from $x_h y_h$
$F / \phi, F_0, N / \nu, N_1, N_2, \beta, t_0, t_1, t_2$	also appear geometrically.		

* Thus $e^{\alpha_1} = \omega / \omega_1$.

2. General Equations for Two Circuits with Reactive Coupling.

The arrangement is shown in fig. 1. An impedance Z_1 is connected to the output side of a valve, while impedances Z_2, Z_3 are connected to the input side. The plate-filament and grid-filament capacities, together with any resistances which may be associated with them, are included respectively in Z_1 and Z_3 . Any impedance Z_0 may be connected between plate and grid, and will include the plate-grid capacity. S represents the internal plate-filament resistance of the valve: an e.m.f. e is injected in series with Z_2 .

The equations for the currents as derived by Miller are :

i_2	i_0	i_1	$\left. \begin{array}{c} \\ \\ \\ \end{array} \right\} = e$	$\left. \begin{array}{c} \\ \\ \\ \end{array} \right\} \cdot (1)$
$Z_2 + Z_3$	$-Z_3$	0		
$-Z_3[\mu + 1]$	$Z_3[\mu + 1] + Z_0 + S$	$-S$		
$-Z_3$	$Z_0 + Z_3$	Z_1		

The determinant may be written :

$$\begin{vmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{vmatrix} \cdot \begin{matrix} . & . & . & . & . & . \end{matrix} \quad (2)$$

The relation between i_2 and e when $Z_2=0$ is given by

$$\frac{i_2}{e} = \frac{\Delta_{11}}{\Delta} = \frac{Z_1[\mu + 1] + S}{Z_1S + Z_0[Z_1 + S]} + \frac{1}{Z_3} \cdot \cdot \cdot \quad (3)$$

Hence, as regards phenomena in the input circuit, the valve and the output circuit which is coupled to it may be replaced by an impedance in parallel with Z_2 and Z_3 . The reciprocal of this impedance is known as the equivalent grid input admittance, which will be referred to as a_{g1} : its value is given by the first term on the right side of equation (3).

Miller's equations (1) are not the most suitable for the development of this paper, and we will use instead equations corresponding to the scheme shown in fig. 2, where impedances are replaced by admittances and the variables are the potential differences e_1, e_2 .

It is easily shown that the following equations hold :—

e_1	e_2	$= e \cdot a_2, \quad . \quad . \quad (4)$
$-a_0$	$a_0 + a_2 + a_3$	
$s_X + a_0 + a_1$	$g_1 - a_0$	

where g_1 is the mutual conductance of the valve.

Figs. 1-5.

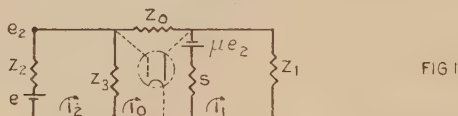


FIG 1

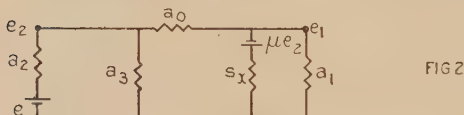


FIG 2



FIG 3

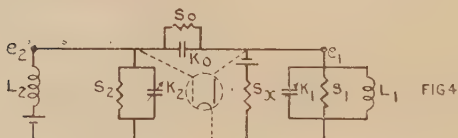


FIG 4

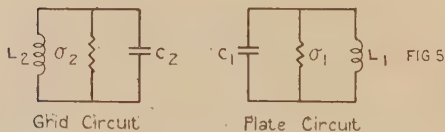


FIG 5

The equivalent grid input admittance a_{g1} (fig. 3) is given by

$$\frac{e \cdot a_2}{e_2} = a_2 + a_3 + a_{g1} \quad (5)$$

But

$$\frac{e \cdot a_2}{e_2} = \frac{-\Delta}{\Delta_{12}} = a_2 + a_3 + a_0 + \frac{a_0 [g_1 - a_0]}{s_X + a_0 + a_1} \quad (6)$$

Hence

$$a_{g1} = a_0 + \frac{a_0 [g_1 - a_0]}{s_X + a_0 + a_1} \quad (7)$$

The voltage amplification from grid to plate is

$$\frac{e_1}{e_2} = \frac{-[g_1 - a_0]}{s_X + a_0 + a_1} \quad \dots \quad (8)$$

The voltage amplification from input to grid is

$$\frac{e_2}{e} = \frac{a_2[s_X + a_0 + a_1]}{a_0[g_1 - a_0] + [s_X + a_0 + a_1][a_0 + a_2 + a_3]} \quad \dots \quad (9)$$

3. Two Resonant Circuits.

We will now develop the special case where both grid and plate circuits are tuned with reactive coupling, as shown in fig. 4.

Comparison with fig. 2 discloses the following identities:—

$$\left. \begin{aligned} a_0 &= s_0 + j\omega K_0, \\ a_1 &= s_1 + j\omega K_1 + \frac{1}{j\omega L_1}, \\ a_2 &= \frac{1}{j\omega L_2}, \\ a_3 &= s_2 + j\omega K_2. \end{aligned} \right\} \quad \dots \quad (10)$$

The voltage amplification is, by (8) and (9),

$$\frac{e_1}{e} = \frac{-a_2[g_1 - a_0]}{[s_X + a_0 + a_1][a_0 + a_2 + a_3] + a_0[g_1 - a_0]} \quad (11)$$

Substituting from (10) and using abridged notation, we have

$$\left. \begin{aligned} a_0 &= s_0 + jK_0\omega, \\ a_2 &= \frac{1}{jL_2\omega}, \\ s_X + a_0 + a_1 &= s_{10X} + j\left[K_{10}\omega - \frac{1}{L_1\omega}\right], \\ a_0 + a_2 + a_3 &= s_{20} + j\left[K_{20}\omega - \frac{1}{L_2\omega}\right], \end{aligned} \right\} \quad \dots \quad (12)$$

where, for example,

$$s_{10X} = s_1 + s_0 + s_X.$$

4. Simplified Notation and Equivalent Circuits.

The composite capacities and conductances which occur with multiple suffices in the preceding equations may now

be treated as single elements, and with this view the notation will be simplified as follows:—

Notation.

$$\begin{array}{l} \text{OLD ... } L_1 \ L_2 \ K_0 \ K_{10} \ K_{20} \ s_{10X} \ s_{20} \ s_0 \ g_1 - s_0, \\ \text{NEW... } L_1 \ L_2 \ C_0 \ C_1 \ C_2 \ \sigma_1 \ \sigma_2 \ \sigma_0 \ g; \end{array} \quad \left. \vphantom{\begin{array}{l} \text{OLD ... } L_1 \ L_2 \ K_0 \ K_{10} \ K_{20} \ s_{10X} \ s_{20} \ s_0 \ g_1 - s_0, \\ \text{NEW... } L_1 \ L_2 \ C_0 \ C_1 \ C_2 \ \sigma_1 \ \sigma_2 \ \sigma_0 \ g; \end{array}} \right\} \quad (13)$$

and equivalent grid and anode circuits will be dealt with: these are shown in fig. 5.

The following symbols will be required to relate the frequency of the impressed wave to that of the resonance frequencies of the circuits in fig. 5:—

$$\left. \begin{array}{ll} \omega_1^2 = \frac{1}{C_1 L_1}, & \omega_2^2 = \frac{1}{C_2 L_2}, \\ m_1 = \frac{1}{\sigma_1 L_1 \omega_1}, & m_2 = \frac{1}{\sigma_2 L_2 \omega_2}, \\ \alpha_1 = \log \frac{\omega}{\omega_1}, & \alpha_2 = \log \frac{\omega}{\omega_2}, \\ t_1 = 2m_1 \sinh \alpha_1, & t_2 = 2m_2 \sinh \alpha_2, \end{array} \right\} \quad . \quad . \quad (14)$$

together with the symbols:

$$p = \frac{C_0 \omega}{g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$N_1 = \frac{\sigma_0 g}{\sigma_1 \sigma_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$N_2 = \frac{C_0 \omega_2 g}{\sigma_1 \omega_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Using the new notation given in (13) and the symbols given in (15, 16, 17), equations (12) become

$$\left. \begin{array}{ll} a_0 = \sigma_0 + jC_0 \omega = \frac{\sigma_1 \sigma_2}{g} \left[N_1 + jN_2 \frac{\omega}{\omega_2} \right], \\ a_2 = \frac{1}{jL_2 \omega} = -jC_2 \omega_2 \cdot \frac{\omega_2}{\omega}, \\ s_X + a_0 + a_1 = \sigma_1 [1 + jt_1], \\ a_0 + a_2 + a_3 = \sigma_2 [1 + jt_2], \\ g_1 - a_0 = g - jC_0 \omega = g[1 - jp]; \end{array} \right\} \quad . \quad . \quad (18)$$

and equation (11) becomes

$$\frac{e_1}{e} = \frac{jC_2\omega_2g}{\sigma_1\sigma_2} \cdot \frac{\omega_2}{\omega}(1-jp) \cdot \frac{1}{(1+jt_1)(1+jt_2) + [1-jp][N_1+jN_2\omega/\omega_2]} \quad (19)$$

This equation is exact.

5. Approximate Expression for Voltage Amplification.

When highly resonant circuits are used the variation of ω over the tuning range is small, and the ratio ω/ω_2 may be put equal to unity where it occurs explicitly in (19), but not where it occurs implicitly in t_1 and t_2 , since there the small quantity $\partial\omega/\omega$ is multiplied by a large quantity m . Again, when a valve is used whose grid-plate capacity is small, p may be neglected. Thus in a valve with the plate electrostatically shielded from the grid by a wire mesh we may have the values :

$$C_0 = 10^{-13} \text{ farad,}$$

$$g = 10^{-3} \text{ amp/volt ;}$$

hence, if $\omega = 10^7$,

$$p = \frac{10^{-13} \times 10^7}{10^{-3}} = 10^{-2}$$

and is negligible. Accordingly (19) may be written in the approximate form :

$$\frac{e_1}{e} = \frac{jC_2\omega_2g}{\sigma_1\sigma_2} \frac{1}{(1+jt_1)(1+jt_2) + N_1 + jN_2} \quad (20)$$

Equation (20) * will form the basis of further development in this paper, but a preliminary discussion of the properties of a single resonant circuit and of two coupled resonant circuits will be necessary before this development can be taken up.

6. Standard Line Diagram.

If a single parallel circuit, such as either of the two shown in fig. 5, be connected to a source of alternating e.m.f. e by terminals placed at opposite ends of the inductance, then the

* In (20), σ_1 and σ_2 are regarded as independent of ω : this approximation may, according to the nature of σ_1 and σ_2 , increase or decrease the error due to putting ω_2 equal to ω .

total current flowing through the circuit is given by *

$$i = e\sigma[1+jt], \quad \dots \dots \dots (21)$$

where the variation of t may be due either to change of capacity with fixed impressed frequency, or to change of impressed frequency with fixed capacity.

Hence the admittance is proportional to the lengths of lines drawn from a point P to a line QR (fig. 6, a). Let PQ, the perpendicular to QR, be the unit length, then PR represents the complex vector $1+jt$. A standard line diagram consists of a line QR associated with a point P at unit distance from it and graduated so that $QR=t$, the tangent of the angle by which the current is in advance of the e.m.f.

Similarly, for a single series circuit where the e.m.f. is injected in series with the inductance,

$$e = iR[1+jt], \quad \dots \dots \dots (22)$$

and the impedance is proportional to PR.

Figs. 6-10.

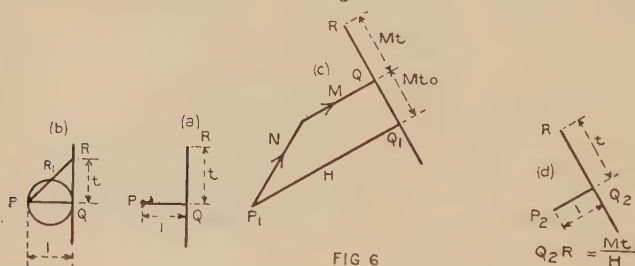


FIG 6

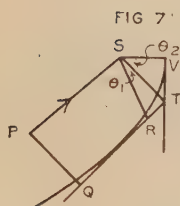


FIG 7

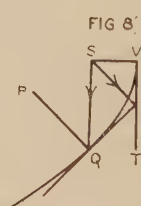


FIG 8

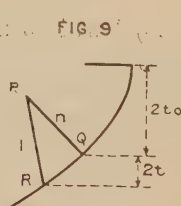


FIG 9

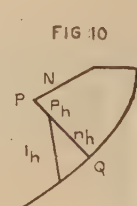


FIG 10

7. Standard Circle Diagram.

By inverting the line QR from the point P with reference to a circle of unit radius (fig. 6, b), a standard circle diagram

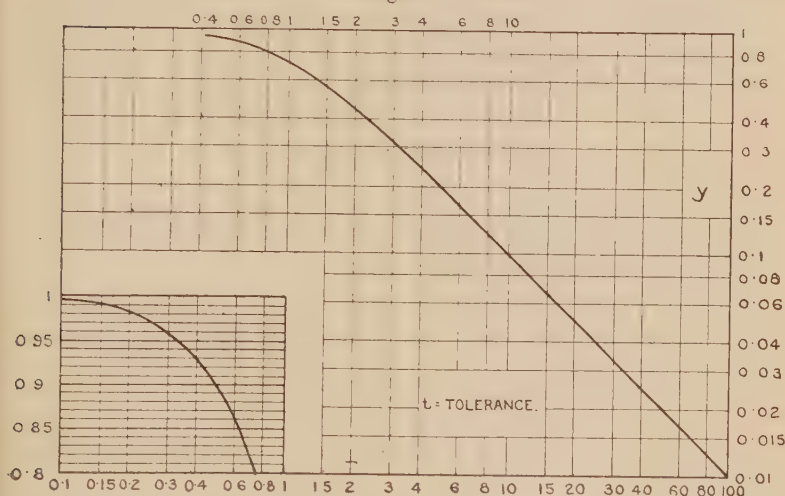
* When the frequency is varied, (21) and (22) are exact if R and σ are regarded as independent of ω : when the frequency is fixed and the capacity is varied, the equations are approximate. The circle diagram and resonance curve discussed in sections 7 and 8 are approximate to the same degree.

is obtained. In the case of a parallel circuit, PR_1 is proportional to the impedance corresponding to a phase-angle t , while for a series circuit PR_1 is proportional to the admittance, or, approximately, to the voltage amplification.

8. Standard Resonance Curve for Single Circuit.

For numerical calculation it is convenient to plot PR_1 as ordinate against t as abscissa (fig. 11). Since any single resonant circuit can be expressed by this curve, it will be termed a standard resonance curve for a single circuit. The

Fig. 11.



abscissa t is the tangent of the phase-angle: it is equal to $2m \sinh \alpha$, or, approximately, to $2m \partial \omega / \omega_0$, where $m \left(= \frac{L\omega}{R} \text{ or } \frac{1}{\sigma L\omega} \right)$ is the voltage amplification factor of the circuit at resonance.

9. Tolerance and Activity.

Since it will appear that standard resonance curves can be used for two circuits reactively coupled, with abscissa $T = Ac \partial \omega / \omega_0$ where T and Ac have no longer the simple signification of t and $2m$, the following nomenclature will be used:—

T = tolerance of circuit,

Ac = activity of circuit,

$$\partial \omega / \omega_0 = \frac{\omega - \omega_0}{\omega_0} = \text{frequency departure.}$$

In the case of a single circuit the tolerance is identical with the tangent of the phase-angle, and the activity is $\frac{2L\omega_0}{R}$ or $\frac{2}{\sigma L\omega_0}$.

10. *Linear Transformation of Standard Line Diagram.*

If the vector $1+jt$, corresponding to PR in fig. 6(a) be transformed to

$$M/\underline{\mu} [1+jt] + N/\underline{\nu}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where M and N are complex vectors, a new vector diagram results (fig. 6, c), comprising a point P₁ and a line PQR. When this diagram is reduced to standard form (fig. 6, d) and the point Q₂ taken as the origin of t ,

$$Q_2R = T = \frac{Mt}{H}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

the line diagram and hence the resonance curve are of the form used for a single circuit, while the activity has been increased M/H times.

11. *Amplification with Two Circuits reactively coupled.*

Returning to equation (20), we write :

$$\frac{e_1}{e} = jA \cdot F/\underline{\phi}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where

$$A = \frac{C_2\omega_2g}{\sigma_1\sigma_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\frac{1}{F/\underline{\phi}} = (1+jt_1)(1+jt_2) + N_1+jN_2. \quad . \quad . \quad (27)$$

A is the maximum voltage amplification obtainable without reaction, *e. g.* with C₀ zero. F/ $\underline{\phi}$ represents the effect due to reaction which enters through N combined with the change of amplification due to detuning the grid and anode circuits, the latter effect entering through $t_1 t_2$.

F₀, the maximum value of the modulus of F/ $\underline{\phi}$, will be termed the reaction factor. F₀ can be found by varying t_1, t_2 being fixed, to give an intermediate maximum of F, and then varying t_2 to give the final maximum F₀. Putting

$t = \tan \theta$, it is easy to show that

$$\frac{1}{F_0} = \sec \theta_0 + N_1 \cos \theta_0 + N_2 \sin \theta_0, \quad . \quad . \quad (28)$$

where

$$t_0^3 + t_0[1 - N_1] + N_2 = 0 \quad . \quad . \quad . \quad (29)$$

and

$$t_0 = t_1 = t_2. \quad . \quad . \quad . \quad (30)$$

12. Graphical Construction for Amplification.

(a) *Fixed impressed frequency : one condenser varied.*

Equation (27) can be expressed graphically. To the parabola $y^2 = 4x$ (fig. 7) a tangent TQ is drawn. If $TV = t_2$,

ST represents the vector $1 + jt_2$, and if $\widehat{RST} = \theta_1$, SR represents $(1 + jt_1)(1 + jt_2)$. Draw PS to represent the vector N : vectorial addition gives

$$PR = PS + SR = \frac{1}{F/\phi}$$

by (27). PQ , the normal to QT , represents $\frac{1}{F_0}$.

When t_2 is fixed, R moves along TQ as t_1 is varied. Hence the line QT and the point P constitute a resonance line diagram of the type given by (23), and the tolerance is given by

$$T = \sec \theta_2 \cdot F_0 \cdot t_1 = \sec \theta_2 \cdot F_0 \cdot 2m_1 \cdot \frac{\partial \omega}{\omega}. \quad . \quad (31)$$

The tolerance curve is that corresponding to a single circuit (fig. 11), and the activity is $\sec \theta_2 F_0$ times that of the anode circuit alone.

(b) *Fixed impressed frequency : both condensers varied.*

With both t_1 and t_2 varied, PQ is minimum when it is a normal to the parabola (fig. 8). It follows by geometry

that $\widehat{QST} = \widehat{VST}$ or $t_1 = t_2$, agreeing with (30), and the ordinate of Q has the value $2t_0 = 2t_1 = 2t_2$ given by (29). Q is the point corresponding to the settings of the grid and anode condensers which give maximum amplification.

$PQ = \frac{1}{F_0}$ and its magnitude is given by (28) and (29) in terms of the coordinates of P .

As P moves towards Q , the activity and voltage amplification increase : instability sets in when P lies on the parabola.

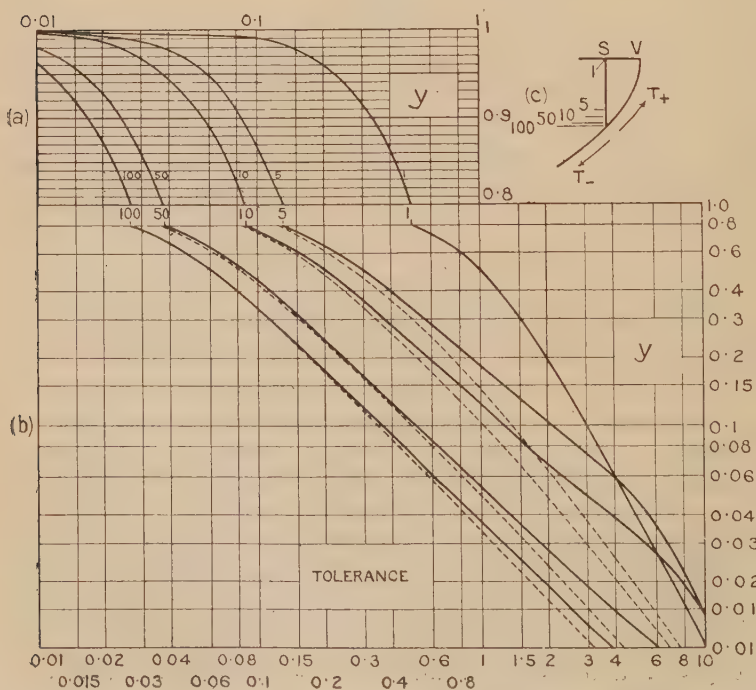
(c) *Impressed frequency varied : both condensers fixed : activities of grid and plate circuits equal.*

The point P being given, let the whole circuit be adjusted to the point Q (fig. 8). As the incoming pulsance is varied from ω_0 its value at Q to some other value ω , the product $(1+jt_0)^2$ will change to $1+j(t+t_0)^2$, where $t=2m\partial\omega/\omega_0$. The locus of the representative point R (fig. 9) will accordingly be the parabola. The resonance curve is obtained by plotting n/l against $t\left(=\frac{l}{n^2}=tF_0^2\right)$. The formula,

$$l_2 F_0^2 = \frac{l^2}{n^2} = T^4 + T^3 [F_0^2 \cdot 4t_0] + T^2 F_0 [6t_0^2 + 4 - 2x] + 1 \dots, \quad (32)$$

can easily be derived *, and is suitable for computation.

Fig. 12.



In fig. 12 resonance curves are given for values of F_0 equal to 1, 5, 10, 50, 100. The locus of P is chosen to be

* The steps are similar to those by which equation (40) is derived from equation (33) when $h=1$.

the latus rectum (fig. 12, c): that is, the coupling is purely capacitative. The full lines correspond to positive, the broken lines to negative, values of T . In fig. 12 (a) the vertical scale is linear, since the logarithmic scale becomes inconveniently cramped near the value unity, and the ordinates are the mean values of the full and the broken lines.

It is evident that the curves are displaced to the left with increasing reaction and that their slope becomes smaller, the latter effect being less marked with negative tolerances. The reason is seen by inspection of the parabola (fig. 12, c). As T increases positively, the vertex is approached and the line l increases more slowly, that is its reciprocal decreases more slowly, than in the negative direction*. The curve $F_0=1$ is, of course, symmetrical.

(d) *Impressed frequency varied: both condensers fixed: activities of grid and plate circuits unequal.*

Let $h = \frac{m_1}{m_2}$, then

$$\frac{1}{F_\phi} = [1 + j(t_0 + t)][1 + j(t_0 + ht)] + N_1 + jN_2. \quad (33)$$

Therefore, putting

$$N_1 = x - 1$$

$$N_2 = -y,$$

$$\begin{aligned} l^2 = \frac{1}{F^2} = & t^4 h^2 + t^3 \cdot t_0 2h(1+h) \\ & + t^2 [t_0^2 (1 + 4h + h^2) + (1+h)^2 - 2hx] \\ & + 2t [1+h] [t_0^3 + t_0(2-x) - y] \\ & + [t_0^2 - x]^2 + [2t_0 - y]^2. \quad (34) \end{aligned}$$

If t_0 is chosen so that $t=0$ when l is minimum, the coefficient of t must vanish; hence

$$t_0^3 + t_0(2-x) - y = 0 \quad (35)$$

(cf. (29): hence t_0 is the parameter of the foot of the normal drawn to the parabola $y^2=4x$ from the point xy).

* This effect is inherent in the nature of reaction: it has no connexion with the asymmetrical resonance curve given by a single circuit of low activity. The activities here considered are so high that the resonance curve (fig. 11) of each constituent single circuit may be taken as symmetrical.

Put $T = t \cdot h^{\frac{1}{2}} F_0^{\frac{1}{2}}, \dots \dots \dots (36)$

$$\frac{1}{F_0^2} = [t_0^2 - x]^2 + [2t_0 - y]^2, \dots \dots (37)$$

$$\beta = 4h/(1+h)^2, \dots \dots \dots (38)$$

$$t_0^2 - x_h = \beta[t_0^2 - x], \dots \dots \dots (39)$$

Then (34) becomes, on multiplying each side by F_0^2 and eliminating t , x , and h ,

$$l^2 F_0^2 = l_h^2 / n_h^2 = T^4 + T^3 \cdot \left[\frac{F_0}{\beta} \right]^{\frac{1}{2}} \cdot 4t_0 \\ + T^2 \cdot \frac{F_0}{\beta} \cdot [6t_0^2 + 4 - 2x_h] + 1, \quad (40)$$

which is of the same form as (32); so that the representative point lies on the parabola $y^2 = 4x$. Hence the construction is as follows (fig. 10).

From the point xy given by the chosen value of N draw the normal PQ to the parabola $y^2 = 4x$. $PQ = n = \frac{1}{F_0}$.

From Q cut off a length $P_h Q = \beta \cdot PQ$, where $\beta = \frac{4h}{(1+h)^2}$.

The resonance curve is now obtained by plotting n_h/l_h against T (T being reckoned from the point Q), where T is connected with the activities of the grid and anode circuits, and with F_0 by the formula

$$T = \sqrt{2m_1 \cdot 2m_2 \cdot F_0} \cdot \frac{\partial \omega}{\omega_0} \dots \dots \dots (41)$$

T , interpreted geometrically, is $F_0^{\frac{1}{2}}$ times the parameter of the parabola, reckoned from Q . The parameter is

$$\sqrt{2m_1 2m_2} \partial \omega / \omega_0,$$

and the coordinates of P , P_h are xy , $x_h y_h$.

For calculation, equation (40) may be used. The activity of the whole circuit is $\sqrt{2m_1 2m_2 F_0}$.

13. *Tabulation of Results.*

The Table summarizes the results so far obtained. If the phase-angle of either circuit changes as the resonance curve is described, the activity of that circuit will appear in the expression for the total activity: F_0 will appear in any case. Thus in the first row in the Table the phase-angle changes

TABLE.

Circuit.	Nature of Resonance Curve.	$\frac{\text{Tolerance}}{\text{Activity}} \times \partial\omega/\omega_0$.	Maximum Voltage Amplification.	Maximum Mutual Admittance.	Parameter of Parabola reckoned from Tuning-point.
Single circuit, impressed frequency varied or condenser varied.	Standard curve for single circuit, derived from circle diagram (fig. 11).	$\Gamma = 2m \partial\omega/\omega_0$.	m .		
Two circuits coupled, impressed frequency fixed : one condenser varied.	Standard curve for single circuit, derived from circle diagram (fig. 11).	$\Gamma = 2m_1 \sec \theta_2 F_0 \partial\omega/\omega_0$.	$m_1 m_2 F_0 g/C_1 \omega$.	$m_1 m_2 F_0 g$.	
Two circuits coupled, impressed frequency varied : both condensers fixed.	Doubly infinite set of curves each defined by a point xy . A few curves shown in fig. 12.	$\Gamma = \sqrt{2m_1 2m_2} F_0 \partial\omega/\omega_0$.	$m_1 m_2 F_0 g/C_1 \omega$.	$m_1 m_2 F_0 g$.	$t = \sqrt{2m_1 2m_2} \partial\omega/\omega_0$.

and the activity appears in column 3; in the second row the phase-angle of the plate circuit only changes and the total activity contains the product $2m_1F_0$; in the third row the phase-angles of both circuits change and the product $2m_12m_2F_0$ appears*.

14. *Effects Due to Reaction.*

When a carrier wave modulated by speech frequencies is received, and it is desired simultaneously to cut out other carrier waves, the slope of the resonance curve should be small over the extent of the side bands due to speech and as steep as possible over the rest of the curve. Reaction in this case will either impair the quality of the speech or eliminate the other carriers less effectively. Further, the curves being asymmetrical, carriers of lower frequency will be more completely cut out than those situated at an equal frequency interval on the higher frequency side.

This effect is shown more clearly by taking for abscissa the ratio of the tolerance for any curve F_0 to the tolerance for the curve $F_0=1$ (fig. 13). As F_0 is increased, the curves become less steep and the asymmetry rises to a maximum and falls again.

When h differs from unity the asymmetry between the grid and plate circuits produces effects similar to those caused by increased reaction. In fig. 14, for any curve F_0 the abscissa is the ratio of the positive tolerance for a given value of h to the positive tolerance when $h=1$. The effect is more marked for small values of F_0 . For $F=100$ the curves are practically vertical lines.

In brief, selective reception from a broadcasting station is best achieved with symmetrical circuits and no reaction, provided that sufficient amplification can be obtained.

* The maximum mutual admittance of two reactively-coupled circuits given in column 5 of the Table is the current flowing across C_1 at resonance per unit e.m.f. injected in the grid circuit: it is obtained from (25) by multiplying each side by $C_1\omega$ and taking the maximum value: it bears a close relation to the expression for the activity given in row 4, column 3.

Under the conditions specified in row 4 the activity will remain constant during any change of the elements of the circuit which leaves the ratio of the mutual conductance of the circuit to that of the valve unaltered, and hence the abscissæ in fig. 12 when divided by this constant activity will represent frequency departures.

Fig. 13.

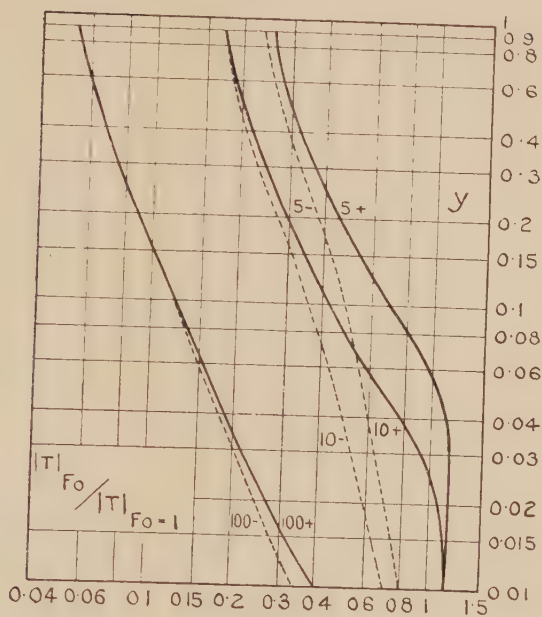
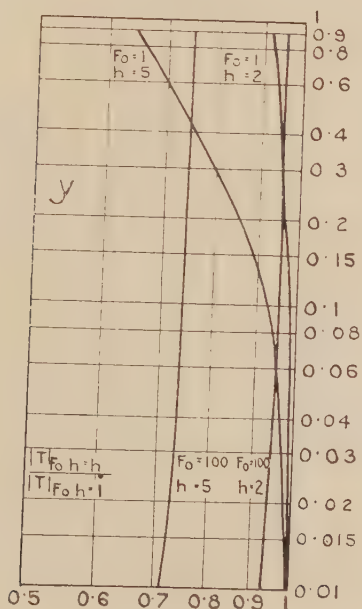


Fig. 14.



15. *General Remarks on Representation by a Parabola.*

For complete representation a doubly infinite set of resonance curves would be required, since one curve corresponds to each point xy . If, however, only one magnitude is required to characterize each curve, such as the ratio of the tolerance when $y=0.9$ to the tolerance when $y=0.01$, a single surface would suffice. In this paper, only a few curves have been drawn for the case of capacitive coupling; any other curve required can be plotted from eq. (40). It may be noted that with capacitive coupling xy lies on the latus rectum and only one normal can be drawn to the parabola, so that the resonance curve has a single peak. It is possible, though the case is of little interest, with values of $\sigma_0/C_0\omega$ of sufficient magnitude to place xy inside the evolute, in which case, since three normals can be drawn, two peaks will appear in the resonance curve*.

The method can also be used for two resonant circuits in a system which contains no source of energy. For example, when two resonant circuits are used with inductive coupling M , the series resistances being $R_1 R_2$, the vector $N=M^2\omega^2/R_1R_2$, and is drawn along the axis of x to the focus. When the activities are equal the resonance curve is symmetrical: critical coupling occurs when $N=1$, and for closer coupling xy lies inside the evolute and the resonance curve shows a double peak.

16. *Explanation of the Systems of Co-ordinates.*

Positive directions of x are drawn towards the *left*, and positive directions of y are drawn upwards, from an origin which coincides with the vertex of the parabola. Vectors have their positive real components drawn to the *right* and their positive imaginary components drawn upwards. Angles increase positively in anti-clockwise direction.

It follows that in figs. 7-10 negative values of t_0 are shown and that the phase-angles θ_1 and θ_2 are negative.

* The value of $\sigma_0/C_0\omega$ may be far from negligible in the case of a valve whose plate is electrostatically shielded from the grid. Taking $\sigma_0=10^{-6}$ mho, $C_0=10^{-13}$ F., $\omega=10^7$, we find $\sigma_0/C_0\omega=1$. Hence N may be inclined at 45° , as shown approximately in fig. 7.

XCIX. *The Effect of Various Flange Systems on the Open-end Correction of a Square Organ Pipe.* By S. A. HIGGS, B.Sc., and L. C. TYTE, B.Sc., Research Students, East London College*.

[Plates XXIII. & XXIV.]

Introduction.

§ 1. [IN 1860, Cavaillé-Coll¹, a French organ builder, showed that the sum total of the lip and open-end corrections to the length of an organ pipe was $2b$, where b is the depth of the pipe—that is, the distance in centimetres from the front, *i.e.* the side containing the lip, to the back of the pipe. Later, in 1906, Brillouin² stated that the $2b$ was the aggregate of $0.4b$ due to the open end, and $1.6b$ due to the lip.

In 1877, R. H. M. Bosanquet³ found that the end correction for a square iron pipe 5 inches long and of 2 inch side was $0.44b$. It is important to note that the pipe he used had its outside edges cut away at each end, so that there was nothing in the nature of a flange on the pipe.

Rayleigh⁴ has calculated the correction for the open end for cylindrical pipes having an infinite horizontal flange to be between $0.82R$ and $0.78R$, where R is the radius, the actual value being nearer the upper limit. He⁵ found that the flange had the effect of increasing the end correction by $0.2R$. This experiment was repeated by R. H. M. Bosanquet⁶, who gives the more correct value of $0.25R$ for the increase in effective length of the pipe due to the horizontal flange. This gives the value of the open-end correction of the unflanged cylindrical pipe as about $0.6R$.

The main purpose of the following work was to test to what extent Rayleigh's analogy with the problem of electrical resistance is applicable to the case of square organ pipes.

Experimental Arrangements.

§ 2. A general view of the apparatus used throughout the whole course of the experiments is shown on Pl. XXIII. fig. 1. The hand-operated bellows in the left background was connected to the acid carboy on the extreme right. The air passed from this through each of the other carboys in turn to the last, which is the one nearest the bellows. From this issued three output pipes, one to the manometer seen on the left of the bellows, and one to each of the organ pipes situated

* Communicated by Prof. C. H. Lees, F.R.S.

about 10 feet apart. It will be seen that the pipes were quite symmetrical about the air-supply. The pressure used for blowing the pipes was 6 cm. of aniline throughout the whole range of experiments, and after some practice it was possible to keep this pressure constant to within about a millimetre. This point is important since it was found that, although the pipes were, for all practical purposes, exactly alike, and the arrangement was, as already mentioned, quite symmetrical, a variation of less than half a centimetre change in the pressure produced a noticeable change in the relative frequencies of the pipes—*i. e.*, the rate at which they were beating.

The pipes were made of wood and were of square cross-section. The approximate dimensions were:—

Length	40	cm.
Depth	3	„
Thickness of walls	1.0	„
Height of lip	0.9	„

It is interesting to note that when a pipe with height of lip 1.1 cm. was compared with one of nominally the same pitch, whose lip was 0.9 cm., the pipes required totally different pressures of blowing in order to sound the fundamental properly, and when thus sounding gave notes quite a semi-tone apart. When both pipes had 0.9 cm. lips, one pipe was about 4 vibrations per second sharper than the other. As some of the flanges which were placed on one of the pipes caused a change in frequency of 6 to 7 vibrations per second, the flanges were placed on the sharper of the two pipes. The flatter was used as the standard, and constant tests were made to see if the other pipe remained the sharper, or if the flange had made it pass through the unison point.

Frequency of the Standard Pipe.

§ 3. The determination of the changes in the open-end correction of the pipe necessitated an accurate knowledge of the frequency of the standard pipe. This was found by tuning a vertical monochord to the pipe. Twenty readings gave an accurate determination of the length of piano wire (60.99 cm.) which gave the same note as the pipe. The tension 8 kilograms weight was known accurately. The linear density of the wire (0.004304 gm. per cm.) was obtained by weighing the same length of wire as gave unison with the pipe measured under the same tension of 8 kilograms weight. This was done by cutting the wire at the

lower bridge, reattaching the weights and cutting at the upper bridge. Thus the linear density, under the conditions of the experiment, was found. The frequency of the pipe was given by the following expression :—

Frequency of pipe

$$n = \frac{1}{2l} \sqrt{\frac{T}{\sigma}}$$

$$= 350.0 \text{ vibrations per second.}$$

Hence we have the frequency of the standard pipe as 350.0 vibrations per second at 16° 2 C.

The Open-end Correction.

§. 4. Before proceeding to determine the change produced by various flanges, it was thought advisable to determine the actual end correction itself. The method employed was one suggested by Professor Lees.

One pipe was closed by a perfectly air-tight plunger and tuned to unison with the standard pipe. The plunger was a wooden rod, with a square block of wood, nearly the size of the pipe, on the end. This was covered on the sides by a piece of baize so that it was a tight fit. The bottom of the block was covered with a surface of matchwood. Before inserting the plunger in the pipe, vaseline was placed on the baize to secure a good air-tight joint. A scale was placed on the rod, and the distance of a cross-wire drawn across the top of the pipe, from a fiducial mark, was measured. The plunger was supported by means of a clamp stand, which was securely fastened to an ordinary adjustable screw table. It was found that there was a slight to-and-fro movement of the plunger, so two clamps and adjustable tables were used. This enabled the observer to adjust the position of the plunger with considerable accuracy, the pipes being tuned to less than 1 beat in 10 seconds. One hundred and forty readings of the length of the closed pipe, which was in unison with the other open pipe, were taken.

We then have, for the open pipe,

$$v/2n = L_1 + C_{(\text{lip})} + C_{(\text{end})},$$

where v is the velocity of sound in air, n the frequency of the pipe, L_1 is the length of the pipe, $C_{(\text{lip})}$ is the lip correction, and $C_{(\text{end})}$ is the open-end correction.

And for the closed pipe

$$v/4n = L_2 + C_{(\text{lip})},$$

where L_2 is the length of the closed pipe.

Assuming the lip corrections to be equal, since the pipes were similar, we have, on subtraction

$$v/4n = L_1 - L_2 + C_{(\text{end})}.$$

L_1 and L_2 could be determined accurately ; thus the accuracy of the value obtained depends upon the accuracy of the values of v and n used.

Now, in the experiments

$$L_2 = \mathcal{L} - (l + R - r),$$

where \mathcal{L} was the total length of the pipe when open, l is the distance from the lower surface of the plunger to the fiducial mark R , and r is the scale reading opposite the top of the pipe ; hence, $l + (R - r)$ is the distance from the bottom of the plunger to the top of the pipe.

$$\text{Now,} \quad \mathcal{L} = 40.68 \text{ cm.}$$

$$l = 9.67 \text{ ,,}$$

$$R = 80.00 \text{ ,,}$$

and an average value of $r = 67.69 \text{ ,,}$

$$\therefore \quad L_2 = 40.68 - (9.67 + 80.00 - 67.69) \\ = 18.70 \text{ cm.}$$

$$\text{Now} \quad L_1 = 40.59 \text{ cm.}$$

$$\text{and} \quad v/4n = 24.42 \text{ ,, ;}$$

$$\text{since} \quad v = 341.9 \text{ metres per second}$$

$$\text{and} \quad n = 350.0 \text{ vibrations per second,}$$

both measured at $16^\circ.2 \text{ C.}$,

$$\therefore \quad 24.42 = 40.59 - 18.70 + C_{(\text{end})}.$$

$$\therefore \quad C_{(\text{end})} = 2.53 \text{ cm.,} \\ = 0.808 \text{ } b,$$

where $b = 3.121 \text{ cm.}$, the mean depth of the pipes.

The mean of all the determinations gave the open-end correction of the square organ pipe to be

$$(0.8088 \pm 0.0013) \text{ } b.$$

This is about double the value obtained by Bosanquet.

§ 5. It has been suggested that the closure of the open end changes the value of the lip correction. This is a problem which is very difficult to investigate, but certain conclusions can be drawn from the results of R. Kœnig's⁷ work on the position of anti-nodes in a large square organ

pipe. He used an open pipe, and also the same pipe closed; hence from his results one can obtain values for the lip and open-end corrections for the open pipe, and for the lip and closed-end corrections for the closed pipe. It must be noted that he found a correction for the closed end; but this was small, and would tend to make the above value a minimum. The values of the corrections are given in Tables I. and II.

TABLE I.—The Open Pipe.

Length of open pipe = 2·33 metres.

Depth of pipe = 0·12 „

Order of partial.	Half-wave length.	Open-end correction.	Lip correction.
	metres.	metres.	metres.
III.	0·90	0·09	0·28
IV.	0·658	0·056	0·246
V.	0·513	0·036	0·198
VI.	0·425	0·057	0·162
VII.	0·365	0·067	0·157
VIII.	0·314	0·043	0·141

TABLE II.—The Closed Pipe.

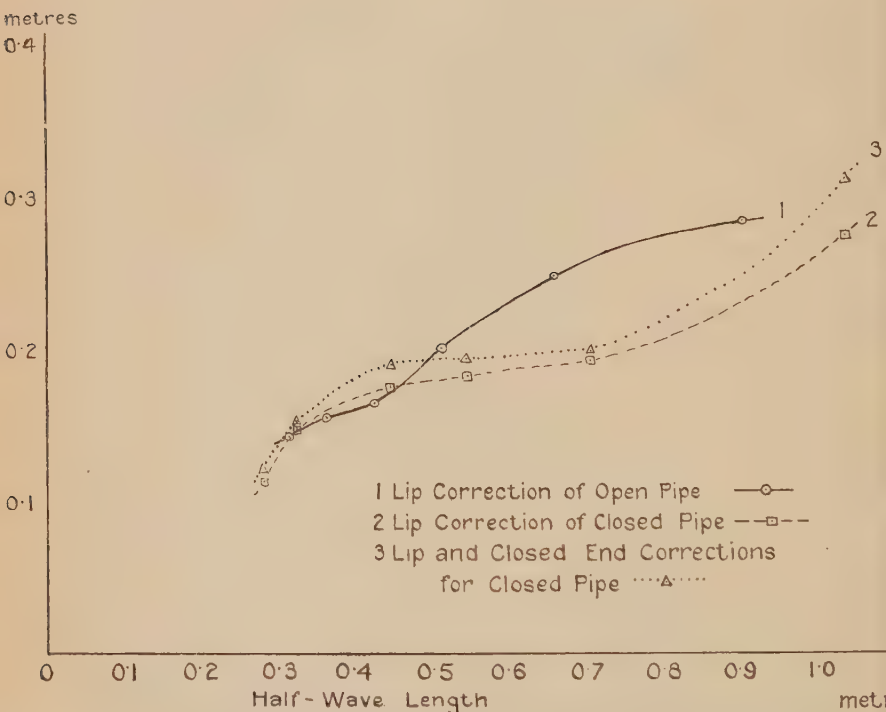
Length of closed pipe = 2·28 metres.

Depth of pipe = 0·12 „

Order of partial.	Half-wave length.	Closed-end correction.	Lip correction.	Total end correction.
	metres.	metres.	metres.	metres.
V.	1·035	0·0375	0·270	0·3075
VII.	0·707	0·0035	0·191	0·1945
IX.	0·549	0·0095	0·182	0·1915
XI.	0·449	0·0145	0·174	0·1885
XV.	0·324	0·007	0·144	0·1510
XVII.	0·282	0·006	0·112	0·118

In fig. 2 the corrections are plotted against the half-wave length of the sound-wave used. In curve I. the lip corrections of the open pipe are plotted, in curve II. the lip corrections for the closed pipe, and in curve III. the lip and closed-end corrections of the closed pipe are plotted. These curves show that there is no considerable change produced in the lip correction by closing the open end of the pipe, and the method of § 4 is justified.

Fig. 2.



Curve plotted between half-wave length $\lambda/2$ as abscissæ and end corrections as ordinates.

The Effect of the "Hopper" Series of Flanges.

§ 6. The next series of experiments was made with "hopper"-shaped flanges, one of which is shown fitted to the pipe on Pl. XXIV. fig. 3. These were made of wood and covered with baize. They were constructed to have a solid angle ω , the semi-angle θ of the triangular section made by

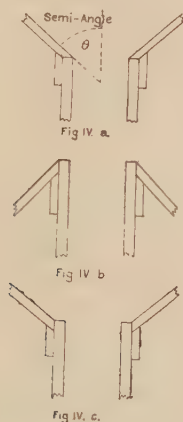
a plane passing through the axis and parallel to one edge being calculated from the formula

$$\omega = 4[2 \cos^{-1}(\sin \theta / \sqrt{2}) - \pi/2].$$

The following flanges were used :—

- (1) A flange of semi-angle 45° , giving a solid angle $2\pi/3$, and 2 feet square at the top ;
- (2) A flange of semi-angle 74° , giving a solid angle $3\pi/2$, and 4 feet square at the top ;
- (3) A plane horizontal flange, giving a solid angle 2π , and 3 feet square ;
- (4) A flange of semi-angle 135° , giving a solid angle $10\pi/3$, being (1) reversed ;
- (5) A flange of semi-angle 106° giving a solid angle $5\pi/2$, being (2) reversed ; and
- (6) A flange of 57° semi-angle, giving a solid angle π , and 2 feet 9 inches square.

Figs. 4 a-c.



The term "hood"-shaped flanges has been given to the reversed "hopper"-shaped flanges. Owing to the desirability of not cutting the pipes themselves, an important distinction existed between the "hopper" flanges and the "hood" flanges. Whereas, with one exception (flange 6), the former were constructed so that their sides met the inside of the square opening (see fig. 4 a), the latter could only have their sides meeting the outside edges of the top of the pipe (see fig. 4 b). Thus these flanges really consisted of

first a small horizontal flange, and then the "hood"-shaped flange round that. With regard to the exception mentioned above, this was the last flange to be made, and was constructed to come down to the outside edges of the pipe (fig. 4*c*). This flange was subsequently remade in the form 4*a* and the readings repeated, a slightly higher value for the change being obtained. The original reading obtained with this flange has been asterisked in Table IV.

As previously indicated, the effect of the flange on the end correction was determined by observing the rate at which the pipes were beating, both when they were in a normal condition and when the flange under consideration was placed on the sharper pipe. A hundred such observations were made for each flange.

It should be mentioned that the change in the open-end correction was calculated from the expression

$$\frac{\text{Change in frequency}}{\text{Frequency}} = \frac{\text{Change in end correction}}{\text{Effective length}}.$$

In most cases the number of beats in an interval of 30 seconds was counted and the number of beats per second calculated. In the following table an extract from a typical set of readings is given, the flange in this case taking the pipes through the unison point:—

TABLE III.—Effect due to "Hopper"-shaped Flange of Semi-angle 45° .

Beats per second without flange.	Means. Beats per second.	Beats per second with flange.	Change. Beats per second.	Residuals.		$\frac{1}{2}$ square of residuals.
				+	—	
4.63	4.48	2.37	6.85	0.12		0.0036
4.33	4.46	2.38	6.84	0.11		0.0030
4.60	4.50	2.07	6.57		0.16	0.0064
4.40	4.45	2.05	6.50		0.23	0.0132
4.50	4.50	1.97	6.47		0.26	0.0169
4.50	4.40	2.27	6.67		0.06	0.0009
4.30	4.34	2.53	6.87	0.14		0.0049
4.38	4.49	2.42	6.91	0.18		0.0081
4.60	4.31	2.47	6.78	0.05		0.0006
4.02						
	503.22	—	807.96	23.67	23.31	6.5203

$$\text{A.M. of change of frequency} = 6.733 \text{ beats per second.}$$

$$\Sigma \frac{1}{4} \text{ square of residuals} = 6.5203.$$

$$\therefore [vv] = 4 \times 6.5203 = 26.0812.$$

$$\therefore \text{P.E. of a single determination} = 0.6745 \sqrt{\frac{26.08}{119}} \\ = 0.31576 ;$$

$$\text{P.E. of A.M. of 120 readings} = \frac{0.3157}{\sqrt{120}} \\ = 0.0288.$$

$$\therefore \text{Change} = (6.733 \pm 0.029) \text{ vibrations per second.}$$

Now, the mean number of beats per second without the flange

$$= 4.1935.$$

$$\therefore \text{Mean frequency of B pipe} \\ = 354.19 \text{ vibrations per second.}$$

Effective length of pipe

$$= \frac{34190}{2 \times 354.19} = 48.27 \text{ cm.}$$

\therefore Change due to flange

$$= \frac{48.27}{354.2} \times \frac{b}{3.116} \times \text{Reduction in frequency,} \\ = 0.04374 \{6.733 \pm 0.029\} b, \\ = (0.2945 \pm 0.0013) b.$$

Further details of the method of calculating the probable error will be found in 'The Combination of Observations' by D. Brunt (Cambridge University Press).

The results obtained with this series of flanges are given in Table IV. In this first line the value of the open-end correction is given ; the walls of the pipe can be considered to be a flange of solid angle 4π .

Approximate Mathematical Theory.

§ 7. Now let us, following Rayleigh, consider these cases from the electrical standpoint. Firstly, we will consider the pipe as cylindrical and to have on its end an infinite conical conductor, the circle of intersection of cylinder and cone

TABLE IV.—Summary of Results.

 b = depth of pipe = 3.116 cm.

Description of flange.	Semi-angle θ of flange.	Angle subtended by flange at opening.	No. beats/sec. without flange (mean).	No. beats/sec. with flange (mean).	Change in no. of beats/sec. due to flange.	Change in end correction as increase in length of pipe.	Total end correction.
"Hopper"	45°	4π	4.194	2.539†	6.733	$(0.2945 \pm 0.0013)b$	0.8088 b
"Hopper"	57°	π	3.891	0.241	3.650	$(0.1599 \pm 0.0014)b$	1.1033 b
"Hopper" *	57°	π	4.143	1.029	3.114	$(0.1363 \pm 0.0006)b$	0.9687 b
"Hopper"	74°	$3\pi/2$	4.330	2.894	1.436	$(0.0627 \pm 0.0005)b$	0.9451 b
Plane horizontal	90°	2π	3.771	2.798	0.973	$(0.0427 \pm 0.0005)b$	0.8715 b
"Hood"	106°	$5\pi/2$	4.260	3.315	0.945	$(0.0413 \pm 0.0009)b$	0.8515 b
"Hood"	135°	$10\pi/3$	4.447	3.834	0.613	$(0.0268 \pm 0.0006)b$	0.8501 b
							0.8356 b

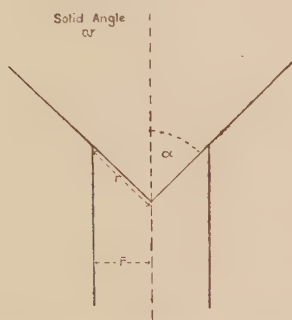
* Reference to this at top of p. 1106.

† With this flange the sharper pipe was flattened through the unison point.

lying on a spherical surface of radius r , whose centre is the apex of the cone (see fig. 5).

Let ρ be the specific resistance of the material, ω the solid angle of the cone, and α the generating angle of the cone.

Fig. 5.



Now the resistance of the cone from the spherical surface r to infinity $= \rho/\omega r$.

Now, if r is the radius of the cylindrical pipe, the resistance

$$= \frac{\rho}{\omega r} \cdot \sin \alpha,$$

$$= \frac{\rho}{\omega \cdot r} \cdot 2 \sin \alpha/2 \cdot \cos \alpha/2.$$

Now, by spherical trigonometry, we know that

$$\omega = 2\pi(1 - \cos \alpha)$$

$$= 4\pi \cdot \sin^2 \alpha/2.$$

Hence

$$\sin^2 \alpha/2 = \omega/4\pi$$

and

$$\cos^2 \alpha/2 = 1 - \omega/4\pi.$$

Hence the resistance

$$= \frac{\rho}{\omega r} \cdot 2 \cdot \sqrt{\frac{\omega}{4\pi}} \cdot \sqrt{1 - \frac{\omega}{4\pi}},$$

$$= \frac{\rho}{r \sqrt{\pi}} \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}.$$

Now the pipe was actually a square one of side b ; so a close approximation is obtained by assuming the cylindrical pipe to be of the same area of cross-section--i. e., $b^2 = \pi r^2$.

Hence the end correction E is the length of the pipe to have the same resistance, and is given by

$$\frac{E\rho}{\pi \bar{r}^2} = r \sqrt{\pi} \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}};$$

$$\therefore E = \sqrt{\pi} \cdot \bar{r} \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}.$$

But $\sqrt{\pi} \cdot \bar{r} = b$;

$$\therefore E = b \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}.$$

The values are calculated for each flange in the following table :—

TABLE V.

Generating angle α .	Solid angle ω .	$\sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}$.	End correction.
45°	$2\pi/3$	$\sqrt{\frac{5}{4\pi}}$	0·6308 b
57°	π	$\sqrt{\frac{3}{4\pi}}$	0·4886 b
74°	$3\pi/2$	$\sqrt{\frac{5}{12\pi}}$	0·3642 b
90°	2π	$\sqrt{\frac{1}{4\pi}}$	0·2821 b

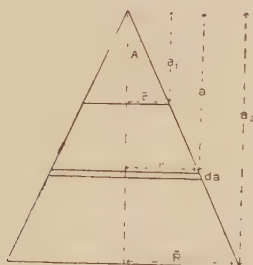
§ 8. Now, secondly, we will consider the electrical analogy of the flange system to be the resistance of a truncated cone of the same dimensions and having its smaller end flush with the pipe.

The resistance is determined as a mean of the lower limit, which is obtained by considering the frustrum of the cone to consist of an infinite number of layers separated by infinitely thin, infinitely conducting disks parallel to the flat ends; and the upper limit, which considers it to be constructed of infinite conical shells separated by infinitely thin, non-conducting layers.

(a) *Lower Limit.*

Consider a frustrum of a cone of generating angle A and of resistivity ρ . Let r be the radius at a distance a_1 along the axis, measured from the apex, and R at a distance a_2 (see fig. 6).

Fig. 6.



Now the resistance of a disk of thickness da at distance a along the axis

$$\begin{aligned} &= \frac{\rho}{\pi} \cdot \frac{da}{(a \tan A)^2}, \\ &= \frac{\rho}{\pi \tan^2 A} \cdot \frac{da}{a^2}. \end{aligned}$$

Hence the resistance of the frustrum of the cone between a_1 and a_2

$$\begin{aligned} &= \frac{\rho}{\pi \tan^2 A} \int_{a_1}^{a_2} \frac{da}{a^2}, \\ &= \frac{\rho}{\pi \tan^2 A} \left\{ \frac{1}{a_1} - \frac{1}{a_2} \right\}, \end{aligned}$$

which is the lower limit of the resistance of the cone.

(b) *Upper Limit.*

As before, consider a cone of generating angle α , solid angle ω , and of resistivity ρ . Now the resistance from a spherical surface of radius r to infinity is

$$\frac{\rho}{\omega r} = \frac{\rho}{2\pi(1 - \cos \alpha)} \cdot \frac{1}{r},$$

since

$$\omega = 2\pi(1 - \cos \alpha).$$

Hence the conductance

$$= \frac{2\pi(1 - \cos \alpha)r}{\rho};$$

therefore the conductance of a conical shell of generating angle α , and of angular thickness $d\alpha$, from the spherical surface of radius r to infinity

$$= \frac{2\pi r \cdot \sin \alpha \cdot d\alpha}{\rho}.$$

Hence the resistance of this shell from spherical surface of radius r_1 to infinity

$$= \frac{\rho}{2\pi r_1 \sin \alpha \cdot d\alpha}.$$

And the resistance of part of it from the spherical surface of radius r_2 to infinity

$$= \frac{\rho}{2\pi r_2 \sin \alpha \cdot d\alpha}.$$

Resistance of shell between spherical surfaces of radii r_1 and r_2

$$= \frac{\rho}{2\pi} \left\{ \frac{1}{r_1} - \frac{1}{r_2} \right\} \frac{1}{\sin \alpha \cdot d\alpha},$$

hence its conductance

$$= \frac{2\pi}{\rho} \cdot \frac{r_1 \cdot r_2}{(r_2 - r_1)} \sin \alpha \cdot d\alpha.$$

Now let us apply this result to the frustrum of the cone. Let C be the apex of the cone of generating angle α , A_1 a point on the right section distance a_1 from the apex, and A_2 a similar point on the right section a distance a_2 from C (see fig. 7).

The conductance of a shell of angular thickness $d\alpha$ between surface A_1 and surface A_2

$$= \frac{2\pi}{\rho} \cdot \frac{CA_1 \cdot CA_2}{(CA_2 - CA_1)} \cdot \sin \alpha \cdot d\alpha,$$

but $CA_1 = a_1 \sec \alpha$

and $CA_2 = a_2 \sec \alpha$;

so the conductance of the shell

$$= \frac{2\pi}{\rho} \cdot \frac{a_1 a_2}{(a_2 - a_1)} \cdot \frac{\sin \alpha \cdot \sec^2 \alpha \cdot d\alpha}{\sec \alpha},$$

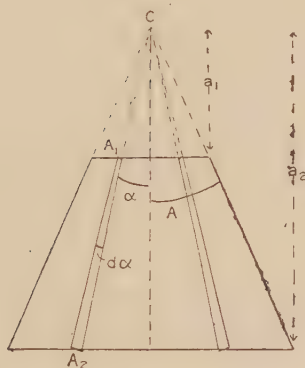
$$= \frac{2\pi}{\rho} \cdot \frac{a_1 a_2}{(a_2 - a_1)} \cdot \frac{\sin \alpha}{\cos \alpha} \cdot d\alpha;$$

\therefore conductance of frustrum of cone of generating angle A

$$= \frac{2\pi \cdot a_1 a_2}{\rho(a_2 - a_1)} \int_0^A \frac{\sin \alpha}{\cos \alpha} \cdot d\alpha,$$

$$= \frac{2\pi a_1 a_2}{\rho(a_2 - a_1)} \cdot \log_e \sec A.$$

Fig. 7.



Hence resistance of frustrum of cone

$$= \frac{\rho}{2\pi} \cdot \left\{ \frac{1}{a_1} - \frac{1}{a_2} \right\} \frac{1}{\log_e \sec A},$$

which is the upper limit of resistance of the cone.

(c) *Mean Value.*

Now we may assume that the tendency for the lower limit to be approached is roughly proportional to the surface area of the plane ends, *i. e.* to

$$\pi \bar{r}^2 + \pi \bar{R}^2$$

$$= \pi (\bar{R}^2 + \bar{r}^2),$$

while the tendency for the upper limit to be approached is

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roughly proportional to the curved surface, *i. e.* to

$$2\pi \bar{R} \operatorname{cosec} A \cdot \frac{1}{2} \bar{R} \operatorname{cosec} A - 2\pi \bar{r} \operatorname{cosec} A \cdot \frac{1}{2} \bar{r} \operatorname{cosec} A \\ = \pi \operatorname{cosec}^2 A (\bar{R}^2 - \bar{r}^2).$$

Hence resistance of lower : upper

$$= (\bar{R}^2 + \bar{r}^2) : (\bar{R}^2 - \bar{r}^2) \operatorname{cosec}^2 A,$$

$$= L : U.$$

Thus we may write an approximate value of the resistance of the frustrum of the cone as

$$\frac{\rho}{\pi} \cdot \left\{ \frac{1}{a_1} - \frac{1}{a_2} \right\} \left(\frac{1}{\tan^2 A} \right)^{\frac{L}{L+U}} \left(\frac{1}{2 \log_e \sec A} \right)^{\frac{U}{L+U}},$$

$$\text{but} \quad a_1 = \bar{r} \cot A$$

$$\text{and} \quad a_2 = \bar{R} \cot A.$$

Hence the resistance is

$$\frac{\rho}{\pi} \cdot \tan A \cdot \left\{ \frac{1}{\bar{r}} - \frac{1}{\bar{R}} \right\} \left(\frac{1}{\tan^2 A} \right)^{\frac{L}{L+U}} \left(\frac{1}{2 \log_e \sec A} \right)^{\frac{U}{L+U}}$$

and the end correction is

$$E = \frac{b^2}{\pi} \cdot \tan A \left\{ \frac{1}{\bar{r}} - \frac{1}{\bar{R}} \right\} \left(\frac{1}{\tan^2 A} \right)^{\frac{L}{L+U}} \left(\frac{1}{2 \log_e \sec A} \right)^{\frac{U}{L+U}} \\ = \frac{b}{\sqrt{\pi}} \cdot \tan A \left\{ 1 - \frac{\bar{r}}{\bar{R}} \right\} \left(\frac{1}{\tan^2 A} \right)^{\frac{L}{L+U}} \left(\frac{1}{2 \log_e \sec A} \right)^{\frac{U}{L+U}}.$$

The calculation of the end correction from this formula is shown in the following tables. Table VI. gives the calculation of the "weight," Table VII. the calculation of the weighted portion of the lower limit, Table VIII. that of the upper limit, Table IX. the calculation of the mean value of the end correction, and Table X. a summary of the theoretical and experimental values.

TABLE VI.—Calculation of "Weights."
 $r = 1.756$ cm. $r^2 = 3.084$.

A.	cosec A.	\bar{R}_r	\bar{R}_r^2	$\bar{R}_r^2 + r^2$	$\bar{R}_r^2 - r^2$	$(\bar{R}_r^2 - r^2) \text{ cosec A.}$	$\frac{L}{L+U}$	$\frac{U}{L+U}$
45°	1.414	34.4 _{cm.}	1183	1186	1180	2330 1186 = 0.3344 3546	2360 = 0.6656 3546	
57°	1.192	47.3	2237	2240	2234	3174 2240 = 0.4138 5414	3174 = 0.5862 5414	
74°	1.040	68.8	4733	4736	4730	5123 4736 = 0.4804 9859	5123 = 0.5196 9859	

TABLE VII.—Weighted Portion of Lower Limit.

tan A.	tan ² A.	$\left(\frac{1}{\tan^2 A}\right)$	$\frac{L}{L+U}$
1.000	1.000	1.000	1.000
1.540	2.372	0.4216	0.6027
3.487	12.16	0.08224	0.2730

TABLE VIII.—Weighted Portion of Upper Limit.

sec A.	log _e sec A.	2 log _e sec A.	$\frac{1}{2 \log_e \sec A}$	$\frac{U}{L+U}$
1.414	0.34635	0.69270	1.4437	1.277
1.836	0.60757	1.21514	0.8250	0.8936
3.628	1.2887	2.57732	0.3880	0.6114

TABLE IX.—Calculation of Mean Value of End Correction.

$\frac{\bar{r}}{\bar{R}}$	$\left(1 - \frac{\bar{r}}{\bar{R}}\right)$	$\left(\frac{1}{\tan^2 A}\right) \frac{L}{L+\bar{U}}$	$\left(\frac{1}{2 \log_e \sec A}\right) \frac{U}{L+\bar{U}}$	$\frac{b}{\sqrt{\pi}} \cdot \tan A \left\{1 - \frac{\bar{r}}{\bar{R}}\right\} \left(\frac{1}{\tan^2 A}\right) \frac{L}{L+\bar{U}} \left(\frac{1}{2 \log_e \sec A}\right) \frac{U}{L+\bar{U}}$
0.05105	0.94895	1.0000	1.277	0.6837 <i>b</i>
0.03713	0.96287	0.6027	0.8936	0.4506 <i>b</i>
0.02552	0.97448	0.2730	0.6114	0.3200 <i>b</i>

TABLE X.—Summary of Results.

Solid angle ω .	Infinite cone theory.	Truncated cone theory.	Experimental results.
$2\pi/3$	0.6308 <i>b</i>	0.6837 <i>b</i>	1.1033 <i>b</i>
π	0.4886 <i>b</i>	0.4506 <i>b</i>	0.9687 <i>b</i>
$3\pi/2$	0.3642 <i>b</i>	0.3200 <i>b</i>	0.8715 <i>b</i>
2π	0.2821 <i>b</i>	—	0.8515 <i>b</i>

§ 9. The above calculations only hold for the "Hopper" flanges, and, of course, the truncated cone theory is not even applicable to the horizontal flange. However, the infinite cone theory can be extended, with considerable error due to the spherical cap at the top of the pipe, to the "hood" flanges.

From the above theory the resistance of the infinite cone of solid angle ω is

$$R \frac{\rho}{\sqrt{\pi}} \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}},$$

R being the equivalent external radius of the pipe, which is now involved.

Hence the end correction E is given by

$$\frac{E\rho}{\pi r^2} = \frac{\rho}{R \sqrt{\pi}} \cdot \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}},$$

$$E = \frac{\bar{r}}{\bar{R}} \sqrt{\pi r} \cdot \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}.$$

$$\text{Now } \sqrt{\pi \bar{r}} = b \quad \text{and} \quad \frac{\bar{r}}{\bar{R}} = \frac{b}{B},$$

where B is the external thickness of the pipe.

$$E = \left(\frac{b}{B} \cdot \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}} \right) b.$$

$$\text{And } \frac{b}{B} = \frac{3.116}{5.083} = 0.613,$$

and therefore the end correction

$$= \left(0.613 \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}} \right) b.$$

The calculation of the end corrections for the two "hood" flanges are given in the following table:—

TABLE XI.—End Corrections of "Hood" Flanges.

ω .	$\sqrt{\frac{1}{\omega} - \frac{1}{4\pi}}$.	$\left(0.613 \sqrt{\frac{1}{\omega} - \frac{1}{4\pi}} \right) b.$
$5\pi/2$	$\sqrt{\frac{2}{5\pi} - \frac{1}{4\pi}} = \sqrt{\frac{3}{20\pi}} = 0.218$	$0.134 b$
$10\pi/3$	$\sqrt{\frac{3}{10\pi} - \frac{1}{4\pi}} = \sqrt{\frac{1}{20\pi}} = 0.126$	$0.077 b$

In the theory of the "hood" flanges no account has been taken of the compound nature of the flange, due to the small plane horizontal flange at the top of the pipe caused by the thickness of the walls, which considerably complicates the conditions for the mathematical problem.

We also have for the infinite plane horizontal flange the value given by Lord Rayleigh for cylindrical pipes, which is $0.82 \bar{r}$.

Now $\pi r^2 = b^2$, and hence this value is $.82 b / \sqrt{\pi} = 0.463 b$.

In spite of the incompleteness of the theory of the "hopper" flanges due to mathematical difficulties and the almost total lack of theory for the "hood" flanges, some correspondence between theory and experiment can be traced.

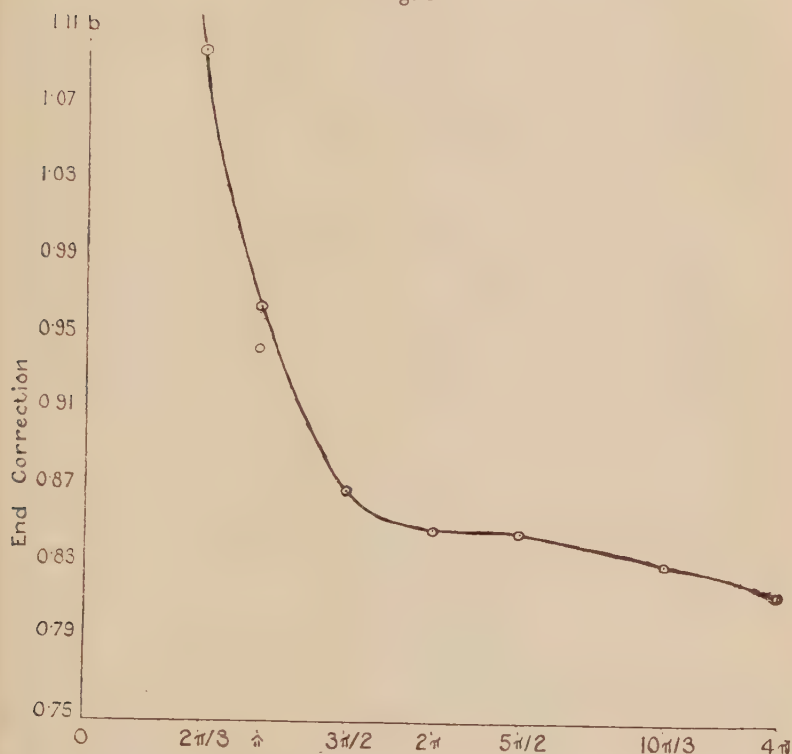
Discussion of Results for the "Hopper" Series of Flanges.

§ 10. It has been shown in Table IV. (p. 1108) that a considerable difference exists in the values of the end correction for the same flange, when firstly it makes contact with the inside of the pipe, and secondly when there is the small plane horizontal flange due to the thickness of the walls of the pipe and then the flange. This emphasizes the importance of the shape of the flange in the near vicinity of the open end of the pipe.

In fig. 8 the experimental values of the end correction have been plotted as ordinates against the solid angles of the flanges as abscissæ. From general considerations it can be seen that for a solid angle 0 the end correction is infinite, and that for a solid angle 4π the flange coincides with the walls of the pipe, and the correction is the ordinary open-end correction. The curve possesses these general characteristics, but the most striking feature is the point of inflexion in the region of the infinite plane horizontal flange. As the thickness of the walls of the ordinary pipe always act as a small horizontal flange, the value of the open-end correction will be higher than it otherwise would be; consequently the value of the change in the end correction will be smaller than it should. Now this effect will not be very serious with a flange of small solid angle, as it will only be a small percentage error; but as the angle of the flange increases, the effect will be more important. When the flanges have solid angles greater than that of the infinite plane horizontal flange, the effect of the small plane flange will play a prominent part, and the observed values of the end correction will be much greater than they should be. Thus the point of inflexion

on the curve is probably due to the effect of the wall of the pipe, and if that had been cut away or a thin pipe had been used, the curve would have been simple with one direction of curvature.

Fig. 8.



Curve plotted between end corrections and solid angle ω .

In fig. 9 the experimental values of the end correction for the three "hopper" flanges are plotted as abscissæ against the theoretical values as ordinates. If the arithmetical mean of the two sets of theoretical values is taken, a straight line can be drawn through the points. Let E be the experimental value and T the mean value on the electrical theory; we have, then, the relationship

$$E = C + kT,$$

both sides of the equation being in terms of b .

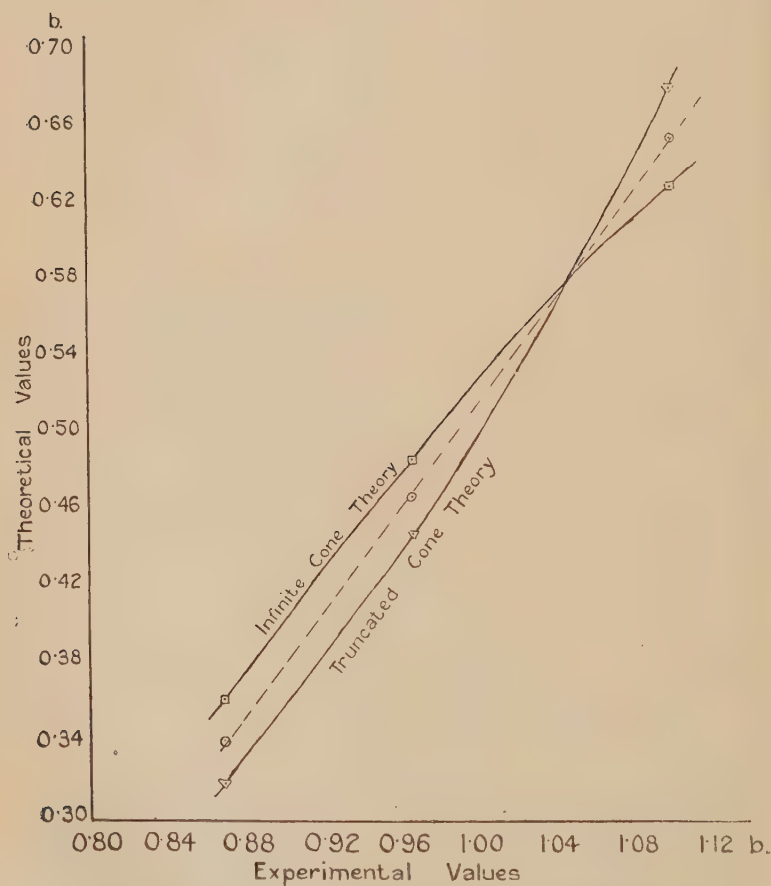
On solving for the constants,

$$C = 0.62 \quad \text{and} \quad k = 0.735 ;$$

hence the expression becomes

$$E = 0.62 + 0.735 T.$$

Fig. 9.



Curve plotted between theoretical and experimental values of end correction.

This gives the relation between the acoustical measurements and the electrical theory. For the open-end correction of the unflanged pipe, whose solid angle is equivalent to 4π , the electrical theory gives the value 0, which is contrary to

common experience. The equation, however, becomes

$$E = 0.62,$$

and hence $0.62b$ can be taken as the open-end correction for an unflanged pipe. [It is lower than the experimental value, as it is the value for the ideal case of a pipe with infinitely thin walls.]

The electrical theory was worked out for cylindrical pipes of equivalent cross-sectional area to the square pipes, on which the acoustical measurements were made; thus the constant $k = 0.735$ may be considered to be the factor necessary to bring the theory into line with the conditions of the experiment.

If this value $0.62b$ is taken as the open-end correction, together with the experimental value of $0.85b$ for the end correction of the pipe with the infinite plane horizontal flange, the change caused by the horizontal flange is $0.23b$; it is interesting to note the correspondence with the values of the end corrections for the cylindrical pipe, which are $0.85r$ for the pipe with an infinite plane horizontal flange, $0.60r$ for the unflanged pipe, and $0.25r$ for the change produced by the flange.

The Effect of the Plane Flanges on the Sides of the Pipe.

§ 11. The final piece of work was an investigation of the effect produced by infinite plane flanges when they were placed on the sides of the pipes, as shown in fig. 1. The flanges used were flat wooden boards 3 feet long by 1 foot 10 inches wide, and covered with baize.

As before, the experiment consisted of counting for a given interval the beats between the pipes alternately without and with the flange in position, one hundred such double readings being taken for each flange.

The first experiment of this series was performed with the vertical flange on and extending 30 cm. down the back of the pipe. An extra piece was fitted on the face of the flange in contact with the pipe to rectify the fact that the flange was not flush with the inside of the pipe, due to the thickness of the wall. [It may be noted in passing that this wedge-like piece was observed to have nearly the same effect as the whole flange.]

It was found that the effect of the flange on the back of the pipe was to increase the effective length of the pipe by
 $(0.1127 \pm 0.0004) b.$

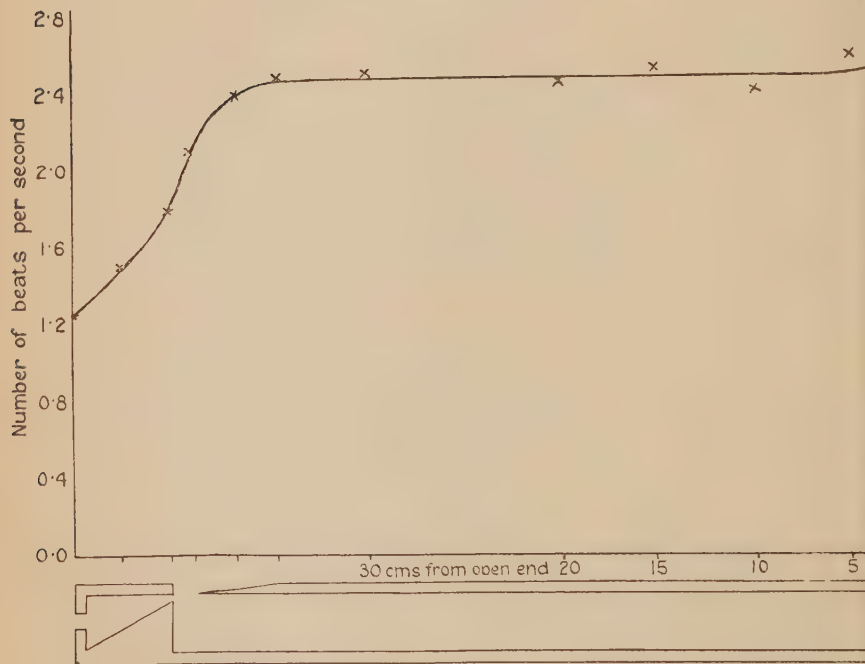
This experiment was repeated with the same flange on the

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side of the pipe. It was found that the effect of this flange
was to increase the effective length of the pipe by

$$(0.1248 \pm 0.0009) b.$$

It was suspected from this difference in values that when the flange was on the side of the pipe it might affect the lip in some way. To test this, determinations of the frequency—by counting the beats with the standard pipe—were made for the flange in various positions down the side of the pipe.

Fig. 10.



Curve plotted between number of beats per second and distance
of flange along pipe.

The results obtained are given in Table XII. In fig. 10 the number of beats per second between the two pipes, for the flange in different positions, are plotted as ordinates, against the position of the lower edge of the flange, measured in centimetres from the top of the pipe, as abscissa.

This portion of the work was completed by investigating the effect of a flange system on one of the back corners of the pipe. It consisted of two flanges joined together at

right angles, each being of the same dimensions as that used in the previous experiments. As in the case of a single flange, a wedge was used to eliminate the effect of the thickness of the walls of the pipe. The effect was observed to be an increase in the effective length of the pipe of

$$(0.2524 \pm 0.0011) b.$$

This value is only 6 per cent. different from the sum of the single flange effects, which is 0.2375 *b*.

TABLE XII.--Number of Beats per Second for Different Positions of the Flange.

Position of bottom of flange.	No. of beats per second.
Bottom of pipe	1.25
Midway between bottom and mouth	1.51
At mouth	1.78
Bottom of lip.....	2.10
Half-way up lip.....	2.41
Top of lip	2.48
30 cm. down from top of pipe.....	2.51
20 " " " " "	2.46
15 " " " " "	2.52
10 " " " " "	2.41
5 " " " " "	2.59
2 " " " " "	2.52
Top of pipe	2.73

Discussion of Results for the Plane Flanges.

§ 12. Let us now consider fig. 10. Firstly, it will be observed that at the 30-cm. point, the position of the flanges in the former experiments, the curve has become quite horizontal; thus we can conclude that when in this position the flange has no effect on the lip. Hence a real difference exists between the effects for a flange on the back and on the side of the pipe; possibly this is due to the fact that at the mouth of the pipe the air moves from the lip in sheets parallel to the front of the pipe, and thereby introduces an inequality in the distribution of the air-flow which still exists at the open end of the pipe. It also shows that the short sleeve connected to the "hopper" flanges had no effect on the lip.

Secondly, it will be noted that the curve slopes steeply upwards in the region corresponding to positions between the bottom and mouth of the pipe. This large change would seem to indicate that the vortices issuing from the lip of the pipe curved right down below the mouth—a fact not generally recognized.

Lastly, the upward sweep of the curve at points corresponding to positions close to the open end points to the fact, previously demonstrated, that the frequency of the pipe is very largely affected by the configuration of its walls close to the open end.

The two sets of flange systems used in this section of the work are the acoustical equivalents of semi and quarter infinite conductors on the electrical theory; and although some of the “hopper” flanges (those of solid angle 2π and π) correspond to these same values, the effects in the acoustical cases are entirely different. Hence we are forced to conclude that the effect depends not only on the solid angle, *i.e.* the amount of free space, but also on the configuration of that free space about the open end of the pipe.

Conclusion.

§ 13. The results can be summarized as follows :—

(1) The value of the open-end correction for a square organ pipe was found experimentally to be $(0.809 \pm 0.001)b$; this value, which is really the one occurring in practice, being higher than that obtained by Bosanquet for a pipe open at both ends. This discrepancy between the results is probably due in part to the effect of the thickness of the walls, and partly to the fact that the length of the pipe used by Bosanquet was $2\frac{1}{2}$ times its breadth, while in the present experiments the length was 13 times the breadth. The estimate of $0.62b$, deduced from the results of the experiments on the “hopper” series of flanges, is probably very near the true value of the open-end correction for an ideal unflanged organ pipe.

(2) In spite of the great difficulties in the mathematical calculations of the electrical resistances, it is possible to make some test of the truth of Rayleigh’s analogy between the acoustical and electrical problems. A study of fig. 9 leads to the conclusion that a linear relation exists between them, and, allowing for the open-end correction, the value in the acoustical case is directly proportional to its electrical equivalent. However, the fact that the effect of the flange system depends not only on the amount of free space it

encloses, but also on the distribution of that free space about the open end of the pipe, shows that in the electrical calculation precautions must be taken to have the lines of flow the same as in the acoustical problem.

(3) The experiments have shown quite definitely that the shape of the flange very close to the opening is very important, suggesting that the transition from the plane waves inside the pipe to the spherical waves, which travel out into free space, takes place rapidly and very near the opening, at a short distance from which the waves have taken up their ultimate form.

In conclusion, these experiments were carried out in the Physical Laboratories of the East London College under the supervision of Professor C. H. Lees, F.R.S., to whom we are greatly indebted for suggesting this work and also for much advice and encouragement during the course of the experiments.

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C. *The Freezing-Points of Concentrated Solutions.*—Part III. *Solutions of Phenol.* By EDWARD R. JONES, Ph.D. (Wales), and C. R. BURY *.

THIS is a continuation of previous work (*Phil. Mag.* (7) iv. p. 841, 1927) on the activity of associated substances in aqueous solution. In this paper are recorded the freezing-points and activities of solutions of phenol, which is unfortunately the only common member of its class which is sufficiently soluble to be suitable for this work.

The phenol used was fractionally crystallized three times, and was then distilled from anhydrous copper sulphate. The purified product was colourless, non-hygroscopic, and

* Communicated by the Authors.

melted at 40.71° C. Solutions were analysed by the method of Redman, Weith, and Brock (J. Ind. Eng. Chem. v. p. 389, 1913): it was found, however, that analyses of the necessary accuracy were only obtained when the phenol solutions used were less than N/20 (*i. e.*, half the strength recommended by these authors). All solutions obtained during the course of our work were stronger than this; hence, after a rough preliminary analysis, weighed quantities were diluted to a known volume so that the resulting solution was as nearly as possible N/20. Duplicate analyses were made in every case, and these usually agreed to within 0.1 per cent.

The method of determining freezing-points has been fully described in a previous communication (Phil. Mag. (7) iii. p. 1032, 1927).

The results are given in the table, where m is the concentration in gram molecules per 1000 grams of water, θ is the depression of the freezing-point, and γ is the activity coefficient (*i. e.*, γm is the activity).

m .	θ .	γ .	M.	x .	K.
0	0		(94.1)	0	
0.1422	0.257	0.948	96.7	0.041	0.765
0.2322	0.412	0.915	98.5	0.067	0.516
0.3065	0.534	0.886	100.3	0.093	0.445
0.3696	0.631	0.858	102.4	0.122	0.439
0.4603	0.768	0.825	104.7	0.153	0.397
*0.5133	0.843	0.804	106.5	0.174	0.391
0.5386	0.881	0.797	106.9	0.179	0.373
0.6213	0.990	0.764	109.7	0.214	0.379
0.6903	1.073	0.737	112.5	0.245	0.399
†0.7803	1.174	0.702	116.2	0.285	0.428

* Eutectic: Ice-phenol hydrate-solution.

† Eutectic: Ice-solid phenol-solution.

The activities have been calculated by the method of Lewis and Randall ('Thermodynamics,' 1923, chap. xxiii.): these authors observe that, in the cases they have studied, the quantity j/m (where $j = 1 - \frac{\theta}{1.858m}$) is independent of concentration at low concentrations, and base their method of extrapolation to zero concentration on this fact. With phenol, j/m appears to be a linear function of the concentration down to the lowest concentration studied: a method

of extrapolation described by one of us (J. Amer. Chem. Soc. xlviii. p. 3123, 1926) is, however, applicable.

It must be remembered that phenol is a weak electrolyte: whilst ionization is quite inappreciable in the range of concentrations studied, it must be perceptible in very dilute solutions. There must therefore be a maximum in the activity coefficient-concentration curve in dilute solution, as with acetic acid, and it is dangerous to extrapolate to more dilute solutions from the data given in the table.

Previous determinations have been made by Peddle and Turner (J. Chem. Soc. xcix. p. 685, 1911) which, except for one point, are in fair agreement with ours; and by Endo (Bull. Chem. Soc. of Japan, i. p. 25, 1926), whose freezing-point in dilute solutions are lower than ours, but agree at higher concentrations. Measurements have also been made by Arrhenius (*Zeit. phys. Chem.* ii. p. 491, 1888) and Rozsa (*Zeit. für Electrochemie*, xvii. p. 934, 1911). Activities have been calculated by Goard and Rideal (J. Chem. Soc. cxxvii. p. 1668, 1925) from the freezing-points of Peddle and Turner: they differ considerably from our values.

Endo (*loc. cit.*) has suggested that the abnormality of phenol is due to association to triple molecules. To test this hypothesis, we have calculated firstly the apparent molecular weight (M) from van't Hoff's equation, taking 1.858 as the molecular lowering of the freezing-point of 1000 grams water. Assuming the change of molecular weight to be solely due to formation of triple molecules, we then calculated the fraction associated (x) and the Law of Mass

Action constant $K = \frac{x}{3(1-x)^3 m^2}$, values for which are given in the table. The constancy of K is hardly satisfactory.

From the data given in the table, it follows that the free energy of formation of one gram molecule of phenol hydrate, $(C_6H_5OH)_2 \cdot H_2O$, from ice and solid phenol at about $-1^\circ C$ is $2RT \log_e \frac{0.5133 \times 0.804}{0.7803 \times 0.702}$ or -306 cal. Free energy is used in the sense defined by Lewis and Randall (*op. cit.*).

One of us (E. R. J.) acknowledges his indebtedness to the University of Wales for a Postgraduate Studentship.

Edward Davies Chemical Laboratories,
University College of Wales, Aberystwyth.
July 19th, 1927.

CI. *The Electrodeless Discharge through Gases.*
*By Sir J. J. THOMSON, O.M., F.R.S.**

ABSTRACT.

THIS paper contains a discussion of the theory of the electrodeless discharge produced when a vessel containing gas at a low pressure is placed inside a solenoid, through which rapidly alternating currents produced by the discharge of Leyden jars are passing. It is shown that to produce the discharge the maximum magnetic force inside the solenoid must reach a value which depends (1) on the nature of the gas, (2) on its pressure, (3) on the frequency of the currents, (4) on the size of the vessel. This value is infinite when the pressure is either zero or infinity, it is a minimum when the pressure is such that $\lambda p = c$, where λ is the free path of the electron in the gas, p the frequency of the alternating current, and c the velocity of the electron when its energy is that required to ionize the gas. Thus there is a critical pressure when the discharge passes most easily, and this depends on the frequency of the currents. Experiments are described which confirm the truth of the theory. It is shown, too, that in the electrodeless discharge very large currents may pass through the gas without producing visible luminosity, so that luminosity of this kind involves processes in addition to the passage of a current. Within a certain range of pressures the gas is in a "sensitive" state, and the discharge has peculiar properties. Within a limited range of pressure and current density striations occur in the electrodeless discharge in hydrogen.

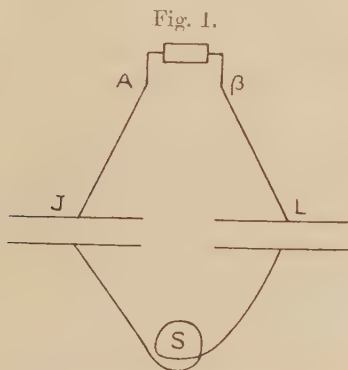
The luminosity at low pressures is not, as it is at high, confined to a ring, but extends on either side forming a double cone with the ring as base; the study of this outlying luminosity leads to very interesting results in connexion with the origin of visible radiation. It is found that the luminosity is quenched by a supply of electrons from a hot wire, and that when a solid is put into it the solid is surrounded by a dark space, which is much thinner than the Crookes' dark space, being only a millimetre or so thick. In many respects it resembles the dark space discovered by Dr. Aston, as it is more freely developed in helium and hydrogen than in other gases, and its thickness does not depend on the pressure of the gas.

Remarkable effects on the discharge itself are produced when certain solids are placed at the centre of the ring

* Communicated by the Author.

discharge. Thus, when a thin deposit on a thin glass rod of platinum or silver, sulphur, or many other substances is placed at the centre of the ring, the discharge is much weakened and may be entirely stopped. On the other hand, other substances such as fused potash, soda, sodium or lithium chlorides facilitate the discharge instead of stopping it; a theory of this effect is discussed, and various chemical effects which are ascribed to very absorbable radiations produced by the discharge are described. Since this type of discharge is exceedingly sensitive to the presence among the normal molecules of a very small number of a different character, whether this difference is due to their being molecules of a different element or to a different energy content of molecules of the same element, it supplies a useful method for studying the properties of these abnormal molecules.

THE type of electrical discharge discussed in this paper was described by me many years ago in the *Philosophical Magazine*, Series 5, xxxii. pp. 321-445. A solenoid S is placed in the circuit connecting the outer coatings of two Leyden jars, J, L, whose inner coatings are connected with *a*, *b*, the terminals of an induction coil. When sparks pass between these terminals electrical



oscillations are started in the circuit, and the solenoid is traversed by rapidly alternating currents; these produce by electromagnetic induction intense electric forces in the neighbourhood of the solenoid. If a glass bulb filled with gas at a low pressure is placed inside the solenoid, *Phil. Mag. S. 7. Vol. 4. No. 25. Suppl. Nov. 1927.* 4 D

these forces produce, when conditions are favourable, a luminous discharge in the form of a ring; this is often exceedingly brilliant and very convenient for many types of investigations.

Mathematical Theory of the Discharge.

Currents passing through the long solenoid produce inside it a magnetic force H parallel to its axis. If no currents pass through the gas H will be constant across the section of the solenoid. In many cases, however, such large currents pass through the gas that they modify the distribution of the magnetic force, screening off as it were from the inside of the discharge tube the magnetic force, due to the currents through the solenoid.

Regarding the gas as a conductor of electricity and assuming for the moment that the conduction follows Ohm's Law, then H satisfies the differential equation

$$\frac{d^2H}{dr^2} + \frac{1}{r} \frac{dH}{dr} = \frac{4\pi}{\sigma} \frac{dH}{dt}, \dots \dots \dots (1)$$

where r is the distance from the axis of the solenoid and σ the specific resistance of the gas.

If the periodic currents due to the discharge of the jars vary as e^{ipt} , equation (1) becomes

$$\frac{d^2H}{dr^2} + \frac{1}{r} \frac{dH}{dr} = \frac{4\pi ip}{\sigma} H;$$

the solution of this is

$$H = AJ_0(nr),$$

where $n^2 = 4\pi ip/\sigma$, and J_0 denotes Bessel's function of zero order. At the outer boundary of the gas, when $r = a$, the magnetic force must be that due to the current through the solenoid, *i. e.* it must be equal to $4\pi NI$, where N is the number of turns per unit length of the solenoid, and I the current produced by the discharge of the jars. Let $H_0 \sin pt$ denote this magnetic force, then

$$H = H_0 \sin pt \frac{J_0(nr)}{J_0(na)}. \dots \dots \dots (2)$$

The number of lines of magnetic force passing through a circle of radius r is equal to

$$\int_0^r H 2\pi r dr.$$

The electromotive force round the circuit is equal to

$$\int_0^r 2\pi r \frac{dH}{dt} \cdot dr,$$

so that the tangential electric force at a point is equal to

$$\frac{1}{r} \int_0^r r \frac{dH}{dt} \cdot dr.$$

The tangential force acting on an electron is due (1) to this force, and (2) to the motion of the electron in the magnetic field; this component is equal to $eH \frac{dr}{dt}$, hence the tangential force acting on an electron is

$$e \int_0^r r \frac{dH}{dt} dr + eH \frac{dr}{dt} = \frac{e}{r} \frac{d}{dt} \int_0^r rH dr.$$

Substituting the value of H from (2) and remembering that

$$xJ_0(x) = \frac{d}{dx} (xJ_1(x)),$$

we see that the tangential electric force on the electron

$$= \frac{e}{r} \frac{d}{dt} \frac{H_0 \sin pt r J_1(\iota nr)}{\iota n J_0(\iota na)}.$$

Hence, if r and θ are the co-ordinates of an electron of mass m and charge e ,

$$\frac{m}{r} \frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) = \frac{e}{r} \frac{d}{dt} \frac{H_0 \sin pt r J_1(\iota nr)}{\iota n J_0(\iota na)};$$

hence

$$r^2 \frac{d\theta}{dt} = \frac{e}{m} \frac{H_0 \sin pt r J_1(\iota nr)}{\iota n J_0(\iota na)}, \quad \dots \quad (3)$$

if $d\theta/dt$ vanishes when $t = 0$.

We have also the equation

$$m \left(\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 \right) = -H e r \frac{d\theta}{dt};$$

hence

$$\begin{aligned} \frac{d^2 r}{dt^2} &= H_0^2 \frac{e^2}{m^2} \frac{\sin^2 pt}{(J_0(\iota na))^2} \frac{J_1(\iota nr)}{\iota n} \left(\frac{J_1(\iota nr)}{\iota nr} - J_0(\iota nr) \right) \\ &= -H_0^2 \frac{e^2}{m^2} \frac{\sin^2 pt}{J_0(\iota na)^2} \frac{J_1(\iota nr) J_1'(\iota nr)}{\iota n}, \quad \dots \quad (4) \end{aligned}$$

We shall now apply these equations to the solution of some special problems.

The first of these is to find the criterion that any discharge should occur in the gas. When the conditions are such that the discharge is only just beginning, the currents passing through the gas are very small, the gas is a very bad conductor, σ is very large, and n very small. When x is small

$$J_0(x) = 1,$$

$$J_1(x) = \frac{x}{2}.$$

Hence from (3) we get

$$\frac{d\theta}{dt} = \frac{e}{2m} H_0 \sin pt,$$

and from (4)

$$\frac{d^2r}{dt^2} + \frac{H_0^2 e^2}{4m^2} r \sin^2 pt = 0.$$

For the discharge to pass, the gas must be ionized; hence the electrons must acquire from the electric field sufficient energy to ionize the gas, and since they lose their energy when they come into collision with a molecule they must get this energy while travelling over a distance less than the mean free path of an electron. Hence, if W is the ionizing potential of the gas, λ the mean free path of the electron, the electrons in a space not greater than λ must acquire a velocity not less than q , where

$$eW = \frac{1}{2}mq^2.$$

But

$$\frac{d\theta}{dt} = \frac{H_0 e}{2m} \sin pt;$$

hence when the velocity $ad\theta/dt$ is equal to q ,

$$q = a \cdot \frac{H_0 e}{2m} \sin pt. \quad . \quad . \quad . \quad . \quad (5)$$

The space passed over in time t is $a\theta$, and thus is equal to

$$\frac{a \cdot H_0 e}{2mp} (1 - \cos pt).$$

This must be equal to λ_1 where λ_1 is not greater than λ ; hence

$$\lambda_1 = \frac{a H_0 e}{2mp} (1 - \cos pt). \quad . \quad . \quad . \quad . \quad (6)$$

From (5) and (6) we get

$$\frac{\lambda_1 p}{q} = \tan \frac{pt}{2},$$

$$\frac{q^2 + (\lambda_1 p)^2}{\lambda_1 p} = \frac{aH_0 e}{m} \quad \dots \dots \dots (7)$$

Thus H_0 , the magnetic force required to produce discharge, will be infinite if λ_1 is either zero or infinite, *i. e.* if the pressure is infinite or zero. It has a minimum value when $\lambda_1 p = q$, and this value is given by the equation

$$2q = \frac{aH_0 e}{m} \quad \dots \dots \dots (8)$$

We see from equation (7) that λ_1 and p only occur in the combination $\lambda_1 p$, so that the magnetic force required for discharge is a function of $\lambda_1 p$, or since λ_1 varies inversely with the pressure P , the magnetic force required for discharge is a function of p/P . This may be compared with Paschen's law for the spark potential when the discharge is between electrodes, *i. e.* that the spark potential is a function of the product of the pressure and the spark length.

This, however, is not the only condition which must be satisfied if the discharge is to occur, for if the electron is to ionize it must after acquiring a certain velocity retain it when under the action of the electric force long enough to enable it to make a collision. Let us suppose that the electric currents through the solenoid are so rapidly damped that only the first vibration is effective. The velocity of the electron will not be less than q from the interval given by the equation

$$q = \frac{aH_0 e}{2m} \sin pt_1 \quad \dots \dots \dots (9)$$

to a time t_2 , where $pt_2 = \pi - pt_1$. During this interval the electron passes over a distance equal to

$$\frac{aH_0 e}{2mp} (\cos pt_1 - \cos pt_2)$$

$$= \frac{aH_0 e}{mp} \cos pt_1,$$

and if it is to make a collision while its energy is great enough to ionize, this distance must be greater than λ , the mean free path of the electron. Hence we must have

$$\frac{aH_0 e}{mp} \cos pt_1 = \lambda_2, \quad \dots \dots \dots (9)$$

where λ_2 is greater than λ_1 . From (8) and (9) we have

$$\tan pt_1 = \frac{2q}{\lambda_2 p},$$

$$a \cdot H_0 \frac{e}{m} = \sqrt{4q^2 + (\lambda_2 p)^2} \dots \dots (10)$$

This, again, makes the minimum value of $aH_0 e/m = 2q$. This, however, only occurs when $\lambda_2 p$ vanishes, and this from equation (7) would make H_0 infinite. Both equations (7) and (10) can be satisfied if we put $\lambda_1 p = \lambda_2 p = q/\sqrt{2}$; this gives for $aH_0 e/m$ the value $3q/\sqrt{2}$, which is only a little greater than $2q$. When there is no damping the conditions expressed by equations (10) and (9) are not required, as if the electron does not make a collision in one oscillation it will do so in another. In this case the discharge will occur when $aHe/m = 2q$. We see from this that even when the damping is so large that only a few vibrations occur very little increase is produced in the magnetic force required to produce discharge.

Since H_0 is given by the equation

$$aH_0 \frac{e}{m} = \frac{3}{\sqrt{2}} q,$$

when the ionizing potential is 12 volts

$$q = 2.1 \times 10^8 \text{ cm./sec.}$$

Since $e/m = 1.8 \times 10^7$; if $a = 5 \text{ cm.}$,

$$H_0 = 4.7.$$

Thus it does not require a very intense magnetic field to produce the discharge.

It is interesting to compare the *electric* force in the electrodeless discharge with that required to produce the spark discharge between electrodes. If F is the electric force for the spark discharge, then the condition that the electron should acquire enough energy to ionize the gas is

$$Fe\lambda = \frac{1}{2}mq^2;$$

if F' is the electric force for the electrodeless discharge

$$F' = \frac{1}{2}a \frac{dH}{dt} = \frac{1}{2}apH_0 \cos pt,$$

the maximum value is

$$F' = \frac{1}{2}apH_0;$$

and since $aH_0 = 2qm/e$ approximately,

$$\frac{F}{F'} = \frac{q}{2\lambda p},$$

when the electrodeless discharge passes most easily,

$$q = \lambda p.$$

Hence $F/F' = \frac{1}{2}$. So that the force in the spark discharge is half the maximum value of the force in the electrodeless.

Variation of the Magnetic Force required to produce the Electrodeless Discharge with the Pressure.

When the pressure is very high $\lambda_1 p$ will be small compared with q , and then from equation (7),

$$aH_0 \frac{e}{m} = \frac{q^2}{\lambda_1 p},$$

since λ_1 is inversely proportional to the pressure of the gas, H_0 will be proportional to the pressure. At low pressures, when $\lambda_2 p$ is large compared with q , we see from equation (10) that

$$aH_0 \frac{e}{m} = \lambda_2 p,$$

so that at very low pressure H_0 varies inversely as the pressure. Thus both at very high and at very low pressures H_0 is very large, the minimum value being at the pressure defined by $\lambda p = q$.

We have supposed that the magnetic force could be represented by the expression $H_0 \cos pt$. In the more general case, when a magnetic field is suddenly produced in the gas, it is easy to see that if this field reaches the value $2qm/ea$ in a time less than λ/q , and persists at this or a greater value for a time greater than λ/q , the conditions for the discharge will be satisfied whatever may be the pressure. Thus the magnetic force required for discharge might remain unaltered over a wide range of pressure, but would increase as soon as the pressure was great enough or low enough to make λ/q either small or large compared with the time taken to establish the magnetic field. Comparatively weak magnetic fields may produce the discharge if they are rapidly established, but however rapidly established they may be they cannot produce the discharge if the maximum value of the magnetic force falls below that given by equation (8).

Electromotive Force round the Circuit.

The electromotive force round the circuit, when $H = H_0 \sin pt$, is equal to

$$\frac{d}{dt} (\pi a^2 H_0 \sin pt) \\ = \pi a^2 H_0 p \cos pt.$$

The maximum value of this is $\pi a^2 H_0 p$. When the discharge passes most easily, $a H_0 \frac{e}{m} = 2q$. Thus the minimum electromotive force which can produce the discharge is

$$2\pi q p a (m/e). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

It is thus proportional to the product of the frequency and the radius of the tube.

If C is the capacity of the Leyden jars used to produce the alternating currents through the solenoid, V the potential to which they are charged when the spark passes, I the current through the solenoid will be given by the equation

$$I = pCV \sin pt.$$

The magnetic force inside the solenoid $= 4\pi NI$, where N is the number of turns of wire per unit length of the solenoid.

$$\text{Hence} \quad H_0 = 4\pi N p C V,$$

$$\text{and since } a H_0 \frac{e}{m} = 2q,$$

$$V = \frac{qm}{2\pi e p N C a}.$$

An approximate value for p is $1/\sqrt{LC}$, where L is the self-induction of the circuit. Substituting this value,

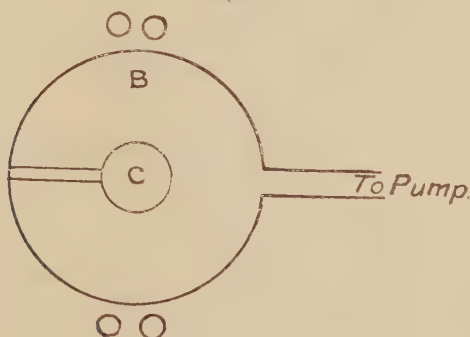
$$V = \frac{q}{2\pi e a N} \sqrt{\frac{L}{C}}.$$

We have hitherto supposed that the currents through the gas were so small that the magnetic forces due to them were negligible compared with those due to the alternating currents through the solenoid; when, however, the electric force due to these currents is much greater than that required to initiate the discharge, the currents through the gas may be comparable with those through the solenoid; the magnetic force produced by the gaseous currents is of the opposite sign to that produced by those through the solenoid, so that the total magnetic force towards the centre

of the tube may be very much less than that due to the currents through the solenoid alone. The following experiment shows this in a striking way.

A bulb C, containing gas at a pressure at which the ring discharge is very easily produced, is placed at the centre of another larger bulb B which is connected with a pump, so that the pressure inside it may be altered. The solenoid is placed round B. When the gas in B is at atmospheric pressure and no ring discharge is visible through it, the ring discharge is very bright in C. On reducing the pressure in B until a bright ring discharge passes through the outer portion of the gas inside it, the ring discharge through

Fig. 2.



C stops. When the pressure in B is still further reduced so that the ring discharge no longer passes through it, the discharge begins again in C. Thus, when the ring discharge is passing through B, the magnetic effect due to the gaseous current is sufficient to neutralize at C the magnetic force due to the current through the solenoid. There is a stage when though there is no discharge in C there is very little luminosity in B, showing that it is possible to have very intense currents with very little luminosity.

The equations already given enable us to calculate the effect of the currents in the gas. The case we have hitherto considered where these effects have been neglected corresponds to very small values of na ; when these effects are very large na is large. Now, if x is large,

$$J_0(\iota x) = \sqrt{\frac{2}{\pi x}} \epsilon^x, \text{ approximately,}$$

and

$$J_1(\iota x) = iJ_0(\iota x).$$

Hence the equation

$$H = H_0 \sin pt \cdot \frac{J_0(\iota nr)}{J_0(\iota na)}$$

becomes, when na and nr are large,

$$H = H_0 \sin pt \cdot \epsilon^{-n(a-r)} \left(\frac{a}{r}\right)^{\frac{1}{2}};$$

as n is very large $\epsilon^{-n(a-r)}$ is very small unless $a-r$ is small, so that the magnetic force will diminish very rapidly with the distance from the surface of the tube.

The equation

$$r \frac{d\theta}{dt} = \frac{e}{m} \frac{H_0 \sin pt \cdot J_1(\iota nr)}{\iota n J_0(\iota na)}$$

becomes, when nr is large,

$$\begin{aligned} r \frac{d\theta}{dt} &= \frac{e}{m} \frac{H_0 \sin pt}{n} \frac{J_0(\iota nr)}{J_0(\iota na)} \\ &= \frac{e}{m} \frac{H_0 \sin pt}{n} \epsilon^{-n(a-r)} \left(\frac{a}{r}\right)^{\frac{1}{2}}. \end{aligned}$$

In order that the electron should be able to ionize the gas the maximum value of $r \frac{d\theta}{dt}$ must not be less than q , hence the condition for the self-sustained discharge is that

$$\frac{e}{m} \frac{H_0}{n} \nless q.$$

The electromotive force round a circuit of radius r

$$\begin{aligned} &= \int_0^r 2\pi r \cdot \frac{dH}{dt} \cdot dr \\ &= 2\pi p H_0 \cos pt \int_0^r \frac{r \cdot J_0(\iota nr)}{J_0(\iota na)} dr \\ &= 2\pi p H_0 \cos pt \frac{r \cdot J_1(\iota nr)}{\iota n J_0(\iota na)}; \\ &= 2\pi p H_0 \cos pt \frac{r \cdot J_0(\iota nr)}{n J_0(\iota na)}, \end{aligned}$$

when nr is large.

Hence the electromotive force round the circuit whose radius is a is

$$2\pi p H_0 \cos pt \cdot (a/n).$$

The maximum value of this is

$$2\pi p H_0 (a/n).$$

The minimum value of H_0 required to sustain the discharge is given by the expression

$$H_0 = \frac{m}{e} nq,$$

hence the maximum value of the E.M.F. round the circuit must not fall below

$$2\pi qap(m/e).$$

This is the same value as when na is small, see equation (11).

Though the E.M.F. round the circuit is the same when na is large as when it is small, the magnetic force is much larger when na is large. For when na is large

$$H_0 = \frac{mnq}{e},$$

and when na is small

$$H_0 = \frac{2mq}{ea};$$

the ratio of the first of these values to the second is $na/2$ and is large since na is large.

Let us now consider the path of an electron. To determine it when na is very small we have the equations

$$\frac{d\theta}{dt} = \frac{H_0 e}{2m} \sin pt,$$

$$\frac{d^2 r}{dt^2} + \frac{H^2 e^2}{4m^2} \sin^2 pt, r = 0.$$

The second equation is a particular case of Hill's or Mathieu's equation, and the solution is not expressed by any simple function. We can, however, from physical considerations get some idea of the path of the electrons.

An electron acted upon by a steady magnetic force at right angles to the direction of projection will describe a circle with an angular velocity equal to $H(e/m)$. Thus, if the frequency p of a variable magnetic force is small compared with $H(e/m)$, the path of the electron will approximate to that which would be described if the magnetic force were constant. In the case we are considering the magnetic force is expressed by $H_0 \sin pt$, hence when $(e/m) H_0 \sin pt$ is large compared with p , the paths of the electrons will be circles. If C is the centre of the cross-section of the

tube an electron starting tangentially from P will, unless interfered with by collision with other molecules, describe a circle on PC as diameter. Thus as the paths of all electrons pass through C, we should expect to find a considerable excess of electrons in the region adjacent to C. The electrons if not in collision move with constant velocity, and thus are just as likely to ionize by collision at one part of the circle as at another. Thus when the pressure is so low that the free path of an electron is an appreciable fraction of the radius of the discharge-tube, the ring discharge may extend to a considerable distance towards the centre of the tube: this is a well-marked phenomenon with the ring discharge. When the pressure is high and the mean free path of the electron a very small fraction of the radius of the solenoid the ring discharge will be confined to a thin ring close to the surface. We see, however, that in any case the electrons will tend to get diffused through the tube, so that when once the discharge has been started other discharges following in rapid succession may expect to find a supply of electrons over the cross-section of the tube. The energy which these stray electrons acquire under the action of the field due to the alternating current through the solenoid will be proportional to the square of the distance from the centre, since their angular velocity is independent of that distance. Thus the electrons nearest the glass of the tube will acquire the greatest energy, and this energy, if the ring discharge is to take place at all, must be not less than the ionizing potential of the gas in the tube. But the electrons nearer the centre of the tube, though they may not acquire enough energy to ionize the gas, may acquire energy greater than that of some of the resonance potentials and so produce luminosity in the gas. As the energy acquired by the electrons decreases as we approach the centre, the luminosity produced in the tube will vary in character with the distance from the centre, the luminosity corresponding to the highest resonance potential occurring nearest the glass of the tube, while at the inner boundary of the luminosity the light will correspond to that with the lowest resonance potential. This effect in some gases is obvious to the most casual inspection, the discharge consisting of rings of different colours at different distances from the centre. When the discharge is examined by a spectroscope the effect is shown by most gases, lines which are prominent in the spectrum of the outer part of the discharge disappearing more or less abruptly as the distance from the centre diminishes.

We have supposed hitherto that the frequency of the electrical vibrations is small compared with $H e/m$. Let us now consider the case where the frequency is very great in comparison with this value. The value of $d\theta/dt$ will now change signs with great rapidity, and so the electron will oscillate from one side to another of a fixed radius, never making more than a small angle with it. We see from the equation that d^2r/dt^2 is always negative, so that the electron will have an acceleration towards the centre of the tube. Thus, the path of an electron in this case will be along a wavy line drawn from its original position to the centre of the tube. This will lead again to a motion of electrons to the centre and their distribution over the cross-section of the tube.

Effect of a Superposed Magnetic Field on the Discharge.

When the magnetic force is that due to the currents through the solenoid, there is a constant phase relation between the direction of the magnetic force and the direction of motion of the electron; the result is, as we see from the equation, that d^2r/dt^2 is always negative, so that the electrons tend to move away from the walls of the tube towards the centre. When, however, there is an external magnetic field parallel to the axis of the solenoid, the radial force on the electron is sometimes in one direction and sometimes in the opposite. It is thus sometimes away from the centre, and when it is so the electrons may be pushed against the walls of the tube before they can ionize the gas; this would stop the discharge from going in one direction. As we shall see, an external magnetic field has a very pronounced effect on the discharge, as this effect is not marked until the magnetic field exceeds a critical value. We can, from experiments on this effect, get some idea of the magnetic forces developed by the currents through the solenoid, as this will presumably be of the same order as the critical external magnetic force.

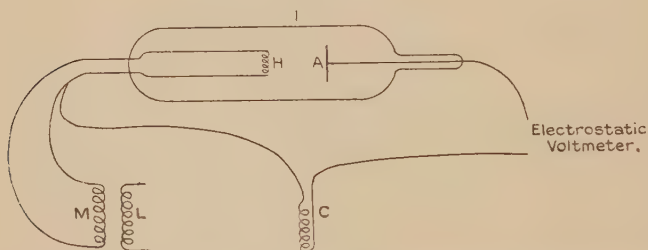
Experiments made to test the Validity of the Preceding Theory.

To test the theory I have made a large number of experiments to see how the electromotive force round the circuit in the discharge-tube when the ring discharge was passing varied with the pressure of the gas, the frequency of the currents through the solenoid, the dimensions of the discharge-tube, and the nature of the gas.

To measure the electromotive force round the circuit, a few turns of thin wire carefully insulated were wound on the outside of the discharge-tube; these were in contact with the outer wall of the discharge-tube and between it and the solenoid. To measure the E.M.F. round this circuit when the discharge was passing, I began by connecting the ends of the circuit to a spark-gap made of two brass balls carefully polished—the distance between the balls was altered by means of a screw, and the distance between them measured by a micrometer. I found, however, that this method was not satisfactory; it was not very sensitive and was somewhat irregular. I discarded it in favour of the method shown in fig. 3.

One end of the circuit was connected with the hot wire H of a large valve, which was very kindly lent to me by the Osram Company. The valve was carefully insulated and

Fig. 3.



the wire was heated by sending an alternating current through the coil L, which induced currents in the insulated coil M, which was in series with the wire. The other terminal A of the valve was connected with one pair of quadrants of an electrometer; the other pair were connected with the other end of the circuit and with earth. The solenoid had a wire soldered to it near the circuit and connected with earth. When the electromotive force round the circuit was in the direction tending to drive negative electrons from the hot wire, electrons would be driven from the wire to A and lower the potential of A and the quadrants of the electrometer connected with it. This process continues until the potential difference between A and earth equals the maximum electromotive force round the circuit in this direction. The reading of the electrometer gave the magnitude of the E.M.F. round the circuit in one direction; the E.M.F. in the opposite direction is not indicated by this arrangement. The electrical oscillations produced by the

Leyden jars are very appreciably damped, so that the E.M.F. in the first oscillation is considerably greater than that in the opposite direction in the second ; thus, when the circuit was connected up so that the first oscillation made the hot wire negative, the reading of the electrometer was considerably greater than if the first oscillation made the hot wire positive; thus, reversing the induction coil made a considerable difference in the reading, as did also reversing the connexions of the circuit with the hot wire valve. In fact, this arrangement gives a very convenient method for measuring the damping of the electrical vibrations. This damping, as has been already stated, is sometimes quite large; it is not uncommon for the electromotive force in the first oscillation to be twice that in the second.

It is essential when using this method to take great precautions to shield the apparatus from external disturbances. Unless this is done it has an uncanny knack of picking up any stray electromotive forces wandering about in the Laboratory ; these, if not eliminated, make the readings irregular. The hot wire valve and the electrometer were placed inside a large box covered with sheet-iron, and the leads from the circuit were surrounded by metal tubes connected with the earth. When these precautions were taken the method worked quite satisfactorily, and gave much more regular results than the spark-gap method.

The following table gives in volts the least E.M.F. round the circuit which will produce at different pressures the electrodeless discharge in air, hydrogen, and helium ; the pressures are given in mm. of mercury, the radius of the bulb was 5 cm.

Air.		Hydrogen.		Helium.	
Pressure. mm. of Hg.	E.M.F. volts.	Pressure. mm. of Hg.	E.M.F. volts.	Pressure. mm. of Hg.	E.M.F. volts.
·018	800	·04	750	·03	920
·13	210	·05	620	·04	920
·185	200	·08	440	·126	720
·280	168	·14	160	·75	120
·410	160	·20	150	1·4	116
·87	200	·32	120	2·1	83
4·0	420	·50	130	3·5	81
		2·1	150	5·4	100
		5·4	300	7·6	108

It will be seen from these figures that graphs representing these results would have very flat maxima, flatter than we should expect if the currents through the solenoid could be accurately represented by the expression $A \cos pt$. The damping of the oscillations is so great that the currents, instead of being represented by a sine curve, are more accurately expressed by a graph, where we have a sudden increase followed by a slower rate of decay. We have seen (p. 1136) that this would give rise to a flat maximum. The minimum E.M.F. round the circuit is found to depend upon the size of the Leyden jars used to produce the alternating currents: it is greater when the jars are small than when they are large. This is in accordance with equation (11), for p is larger with small jars than with large ones. The flatness of the maximum makes it difficult to determine the pressure at which the discharge passes most easily, but the results given above show quite clearly that it is very much higher for helium than for air or hydrogen. The measurements with different sized jars show that this critical pressure increases with the frequency, and measurements with discharge-tubes of different sizes show that the critical pressure does not depend upon the size of the tube.

The effect of pressure and frequency on the discharge can be shown qualitatively in the following way:—A battery of 12 equal small inductances is arranged so that any number from 0 to 12 can be thrown in series with the solenoid; this alters the inductance in the discharging circuit of the Leyden jars, and therefore the frequency of the electrical oscillations. The brightness of the electrodeless discharge is observed when 0, 1, 2, 3, 4, ... inductances are added to the circuit. There is a wide range of pressures when the brightness of the discharge increases as the first few coils are added, but begins again to decrease when the number added exceeds a certain value; thus we see that at a constant pressure there is a certain frequency at which the discharge passes most easily. Again, we find that the number of coils when the discharge is brightest depends on the pressure of the gas: the lower the pressure the greater the number of coils, and therefore the smaller the value of p when the discharge is brightest. This is in accordance with the equation $p\lambda = q$, where p is the frequency, λ the mean free path, and q the ionizing velocity.

According to equation (11) the minimum value of the E.M.F. which can produce discharge is $2\pi qpa(m/e)$. In the experiments recorded in the table $a = 5$ cm.; the minimum

voltage in hydrogen seems to be about 120 volts. If the ionizing potential for hydrogen is taken as 12 volts, $q = 2 \times 10^8$, since $e/m = 1.8 \times 10^7$, p must be 4×10^7 , which is not an unreasonable value as the jars were large and the leads long.

Estimation of the Amount of Ionization Produced in the Gas by the Electrodeless Discharge.

The shielding effect described on p. 1137 enables us to form some estimate of the number of electrons in the gas, and hence of the extent to which the gas is ionized. For we find that when the gas is showing this effect the magnetic force due to the solenoid may be increased to a considerable multiple of the value which would produce discharge in the inner bulb if there were no shielding without any discharge occurring. This shows that the shielding due to the currents passing through the gas reduces the magnetic force in the inside of the bulb to a fraction of that due to the current through the wires of the solenoid; but to do this, the gas currents must be pretty nearly as big as those through the wire.

If n is the number of electrons per unit volume, v their velocity, the current flowing through unit area of the gas is nev ; if H is the magnetic force, v is of the order $rHe/2m$; hence the current through unit area of the gas is $ne^2rH/2m$, but H , the force due to the solenoid, is $4\pi I$, where I is the current flowing through the wires of unit length of the solenoid. Hence the current through unit area of the gas must be of the order $4\pi Ine^2r/2m$; but since these currents are nearly as large as I , $4\pi ne^2r/2m$ cannot be a small quantity if the area through which currents flow is comparable with 1 sq. cm.; as e^2/m is about 3×10^{-13} , n must be of the order 10^{-13} to account for the shielding.

Thus when the shielding occurs at pressures comparable with .001 mm., the number of electrons is of the same order as the number of molecules in the gas, so that a large proportion of these must be ionized.

The effect of pressure on the shielding effect may be shown by the apparatus represented in fig. 2. Beginning with the gas in the outer bulb at atmospheric pressure and gradually reducing the pressure, there is no visible change in the brightness of the discharge in the inner bulb and no visible discharge in the outer until the pressure in the outer tube is of the order of a millimetre. This pressure depends on the nature of the gas: it is much higher for helium than

for hydrogen and higher for hydrogen than for air. On diminishing the pressure below this value the discharge in the inner bulb disappears, though there is but little luminosity in the outer. When the pressure is still further reduced there is often a recrudescence of the luminosity in the inner bulb; this, however, only extends over a small range of pressure. On further reduction the luminosity in the inner bulb disappears again, the luminosity in the outer begins to increase and soon becomes very bright, disappearing again when the pressure gets very low, when the discharge appears again in the inner bulb.

The relation between the luminosity in the inner bulb (the ordinate) and the pressure (the abscissa) is of the type represented in fig. 4. We see that at A there is a range of pressure

Fig. 4.



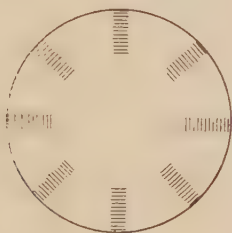
where the currents through the gas are less than at pressures on either side of the range. The properties of the gas in this range of pressure are peculiar: the gas is in the "sensitive" state, of which more will be said later on, and the discharge in this stage, and in this stage only, spreads from the outer bulb through all the tubes connected with it and also through the pump. One fact brought out very clearly by these experiments is that there is very little connexion between the brightness of the electrodeless discharge in the outer tube and the shielding it produces. The shielding effects depend on the currents through the gas. The fact that there may be large shielding with very little luminosity shows that large currents can pass through the gas without producing visible light, and that the production of this depends upon something in addition to the passage of the current. This is borne out by many familiar effects produced when the

ordinary discharge passes between electrodes, for though the average current passing through the different parts of the discharge-tube must be the same, the visible luminosity may be small in some places such as the dark space next the cathode and the dark spaces between the striations, and quite bright in others such as the negative glow and the positive column.

Striations in the Electrodeless Discharge.

On many occasions when the ring discharge was passing through hydrogen it was observed that the luminosity in the ring was not uniform but showed periodic variations, giving it a striated appearance as in fig. 5, the divisions between the

Fig. 5.



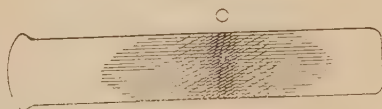
bright and dark portions being radial. This phenomenon only occurs within narrow limits both of pressure and of the intensity of discharge; the bright and dark portions are not steady, but flicker about so that it is not possible to photograph them. The striations are much more pronounced in hydrogen than in any other of the gases I have tried—indeed, I have not been able to feel sure that the phenomenon occurs in other gases.

Another quite different type of striation occurs at suitable pressures and intensities when two equal coils in series are placed at some distance from another on a straight tube containing gas at a low pressure. When the alternating current passes through the coils each coil gives rise to a ring discharge; by adjusting the distance between the coils and the pressure of the gas the luminosity between the coils can in hydrogen be got to show several alternations in brightness. Between the coils the discharge appears to be striated. It is not, however, easy to get the discharge into this state.

Another very interesting effect is observed much more easily. When the pressure of the gas is low the luminosity

in the neighbourhood of the coil of wire carrying the alternating current has the appearance represented in fig. 6: brightly luminous cones stretch out to a considerable distance on either side of the coil. If now two such coils are placed in series along a straight cylindrical tube, at a distance less than twice the length of a cone, the two cones will not blend unless the two coils are very close together, but will be

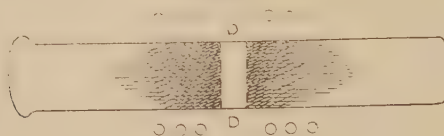
Fig. 6.



separated by a well-defined dark space D, the discharge having the appearance shown in fig. 7. The effect is not so plain at very low pressures as it is at somewhat higher ones.

If, instead of using two coils, we use one coil which can be moved along the tube, and put across one part of the tube a solid plate, either metallic or non-conducting, then, when the coil is moved so that the cone would strike against the plate if it retained its original length, it is found that the cone will never reach up to the plate but will be separated from it by a well-defined dark space. This is more striking in hydrogen and helium than it is in other gases, but I have seen it quite distinctly in air and oxygen. The thickness of this dark space does not, like the Crookes' dark space, increase as the pressure diminishes; it resembles the much thinner dark space discovered by Dr. Aston in helium and hydrogen in

Fig. 7.



being little affected by the pressure. It is, however, much more definite when the pressure is a considerable fraction of a millimetre of mercury than when it is much less than this. The thickness of the dark space depends on the intensity of the ring discharge: it is greater when the intensity is small than when it is great. The dark spaces produced in this way are only a millimetre or less in thickness. We can produce much more extensive dark spaces by letting the luminous

cone strike against a thin tungsten filament which can be raised to incandescence. When the filament is cold the luminosity envelopes the filament, and the only dark space is a very thin layer surrounding the thin filament. When, however, the filament is raised to incandescence and made to emit electrons, the luminosity disappears from a considerable volume around the filament, and there is a large dark space which disappears when the filament gets cold. This experiment suggests that free electrons can destroy the luminosity of the discharge. I think that the dark spaces we have described are due to an effect of this kind rather than to one of a hydrodynamic character due to the presence of the solids or to opposing streams of gaseous molecules. Let us take first the dark space between two cones. Outside each cone there seems to be a distribution of free electrons, so that when one cone is pushed up against a second the first brings a swarm of electrons against the luminosity of the second and destroys it in the front layer, while the electrons accompanying the second cone act in a similar way on the luminosity of the front layer of the first cone. Again, in the case of the solids there may be two effects present: the electrons in front of the cone may strike against the solid and rebound into the luminosity of the cone and destroy it; in addition to this, the electrodeless discharge is the source of very intense ultra-violet radiation. When this falls upon the solid it will make it emit electrons, and these will tend to destroy the luminosity in the neighbourhood of the plate.

The electrons on this view act as absorbers of the energy in the atoms or molecules, which in their absence would be converted into visible radiation.

This effect of electrons on luminosity is in accordance with the view, for which there is much experimental evidence, that the luminosity of a gas depends (1) on its atoms or molecules being put in a state, the "excited" state, in which, though they have more energy than when in the normal state, they are in quasi-stable equilibrium, and (2) on the atoms returning from this state to the normal one and giving out the excess of energy in the form of radiation.

When the atom is in the excited state it is probable that it is more active chemically than when it is in the normal one. One reason for this is that its electrostatic moment is greater; it is more polar, and therefore more likely to unite with an electron. If, however, it forms an association with an electron, which need only last for the very short time during which the atom remains in the excited state, the system with the attached

electron, differing fundamentally from the uncharged excited atom, will not emit radiation of the same type—indeed, it may not give out any visible radiation at all. This effect of electrons on luminosity seems analogous to the very remarkable effects discovered some years ago by Professor R. W. Wood. He found that traces of foreign gas, especially strongly electromagnetic ones, diminish to a remarkable extent the luminosity excited in other gases by resonance. They might, on the view just given, be expected to do this if they formed temporary compounds with the excited molecules of the luminous gas.

Sensitive State of the Ring Discharge.

The electrodeless discharge at certain pressures and intensities is very much affected by the approach of a conductor, though in general this produces very little effect. I have found this effect especially conspicuous in cyanogen, though it exists to some extent in all the gases I have tried. The following description relates to a bulb about 5 cm. in radius filled with cyanogen. When the pressure was much less than .1 mm. of Hg, the ring discharge was very bright and was not sensitive to the approach of a finger. When the pressure was raised to a pressure approaching .1 mm. a stage was reached when the appearance of the discharge suddenly changed with the pressure. Luminosity spreads through the tubes connecting the discharge-vessel with the pump, and if a finger is placed against one of these tubes the luminosity is repelled and there is a dark space under the finger. As I have already stated the shielding effect is abnormal when the gas is in this state. The ring became much less sharply differentiated from the rest of the bulb than it was at lower pressures, and in addition to the ring a bright line of light passing through the centre of the bulb and at right-angles to the ring appeared. When the pressure was still further increased the bright line through the centre broke up and several ill-defined luminous pencils, symmetrically distributed round the axis of the tube, took its place. At still higher pressures these beams disappeared.

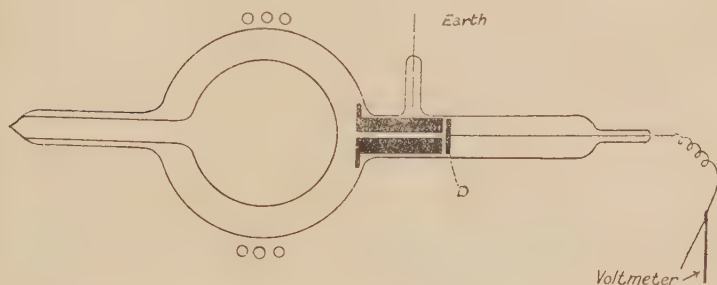
When the bright line was present the discharge was very sensitive to the approach of a finger; it was much brighter when the finger was held near the tube than when it was taken away. If the finger touched the glass the bright beam seemed to reach the glass too, but if the finger stopped short of the glass the beam stopped short too, and could be made

to contract or elongate by moving the finger backwards and forwards. At pressures of about $\cdot 05$ mm. the discharge was in such a sensitive state that unless the finger approached within a certain distance of the bulb there was no discharge of any kind, ring or straight line; a difference of half an inch in the position of the finger would make all the difference between a very bright discharge and none at all.

The bright line through the centre was bent by a magnet, showing that there is a stream of electrons along it. The direction of bending showed that the electrons were moving from the walls of the tube towards the centre.

When the discharge is sensitive the luminosity spreads from the vessel through which the discharge takes place through all the tubes connecting this vessel with the pump.

Fig. 8.



The finger appeared to repel this luminosity from the part of the tube to which it was applied.

If, when the discharge is in this state, a finger be placed against the outer bulb in the apparatus shown in fig. 2, a patch of green phosphorescence, due to cathode rays, will appear on the glass of the inner bulb. The luminous ring in the outer bulb is less differentiated in luminosity from the gas in its neighbourhood than it is outside this range of pressure, and the glass surface of the inner bulb is covered with a luminous glow. Again, as the following experiment shows, the electrical condition of the gas in the outer tube is exceptional over this range of pressure. A tube fitting round a metal rod with a hole in it was fused on to the outer bulb; behind the tube was a disk D connected with a gold leaf electroscope. When the electrodeless discharge was passing at pressures on either side of the sensitive state it discharged with great rapidity any charge, either positive or negative,

in the electroscope, even though this was connected with a Leyden jar to give it greater capacity, but when the discharge was sensitive, though the electroscope lost with great rapidity a negative charge, it did not lose a positive one unless this was in excess of a certain value, and if the electroscope was uncharged to begin with it soon acquired a positive charge. The conditions indicated that this was due to charged ions rather than to a photoelectric effect. There thus seems to be a range of pressure in which there is an excess of positive over negative ions. This would explain the phosphorescent patch produced when the finger is placed against the glass and the glow on the inner bulb, and in fact all the properties of the sensitive state.

The excess of the positive charge over the negative can be explained by the diffusion of electrons to the walls of the tube being more rapid than that of the positive ions. The electrons and the ions disappear from two causes, diffusion and recombination, but since the combination of an electron and a positive ion does not alter the total charge of electricity in the gas, the rate at which the excess of positive charge in the gas increases is equal to the rate at which electrons diffuse to the walls of the vessel. This rate vanishes when the pressure vanishes because then the number of electrons vanishes; it also vanishes when the pressure is very high because then the coefficient of diffusion vanishes. The rate must therefore be a maximum at some intermediate pressure, and it is in the neighbourhood of this pressure that the discharge is in the sensitive state.

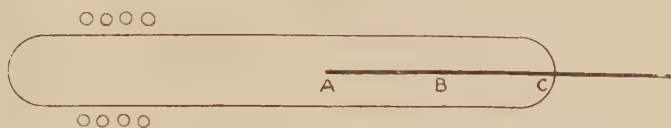
*Influence on the Discharge of various Solid Bodies
in the Discharge-Tube.*

I have observed some curious and suggestive effects produced by the presence of various substances in the discharge-tube. Thus, when making the experiment (described on p. 1149) on the effect of the hot tungsten filament on the luminosity of the discharge in its neighbourhood, I noticed that often when the solenoid produced a bright discharge when at one end of the tube, yet when it was moved down towards the other end of the tube so as to enclose the leads of the filament, which were two wires parallel to the axis of the tube and close together, the discharge stopped completely. This effect differs from the local effect produced by the filament on the luminosity in that the complete stoppage of the discharge is more marked when the tungsten filament is cold than when it is hot, whereas the effect on the luminosity is very much greater for the hot filament than for the cold.

I next tried the following experiment. The discharge-tube was a long cylindrical tube along which the solenoid could be moved from end to end. A thin cylindrical rod of aluminium, about 2 mm. in diameter, ran along the axis of a portion of the tube. When the solenoid did not enclose the rod the discharge went quite freely, but was dimmed when the solenoid was moved down the tube so as to surround the rod. It was easy to adjust the spark-gap in the primary circuit so as to make the discharge quite bright when the solenoid did not enclose the circuit and vanish when it did.

I next replaced the aluminium rod by a fine glass one; one half (AB) of this rod was silvered, the other half (BC) was platinized. It was found, within certain limits of pressure and spark length in the primary circuit, that a bright discharge occurred when the solenoid did not enclose the glass rod, but ceased when it came over the silvered or

Fig. 9.



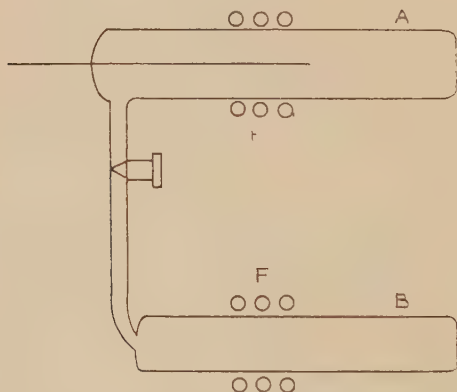
platinized portion. The platinized portion seemed more active than the silver, for when the discharge was quite extinguished when the coil was over the platinum it sometimes still lingered when it was over the silver.

I next, instead of coating the glass rod with metal, used one, half of whose length was clean while the other half was covered with sulphur. I found this produced even more marked results than the platinized one. For the discharge was brightly luminous when the solenoid did not enclose the rod, stopped when it enclosed the sulphur portion, and went again when the solenoid came over the uncovered part of the rod. When the gas in the tube was either hydrogen, air, or nitrogen there was a rapid diminution in the pressure, showing that chemical combination was going on, but the effect just described occurred also when the tube was filled with helium, when there was no change in the pressure.

With this rod in the tube it was found impossible, whatever might be the gas filling, to maintain the discharge for long, even though the solenoid did not encircle the rod. Though the discharge might be bright to begin with it gradually got fainter, and in a few minutes disappeared. Sometimes it was found impossible to get the discharge to

start again however much the spark-gap in the primary circuit was increased. If the tube was left for some hours, or if a current of gas was drawn through it for some minutes, it recovered its power of giving a luminous discharge. The effect seems to be connected with something condensed on the glass walls of the tube, for if the tube be heated for some minutes with a gas flame it recovers its power of giving a bright discharge. If one-half the tube has been heated, while the other half has been left cold, the discharge will often pass when the solenoid is over the part which has been heated, but will not do so when the solenoid is over the other portion. This experiment illustrates the large effects which may be produced by the walls of the tube. To investigate the matter further I tried the experiment represented in fig. 10.

Fig. 10.



A and B are equal cylindrical tubes round which solenoids E and F, equal in every respect, are placed in series. A and B are connected by a piece of quill tubing with a tap between A and B, so that the two tubes can either be shut off from each other or put in communication. The tube A contains a thin glass rod, half of which is coated with sulphur. The tube B contains nothing but the gas with which the tube is filled. Before the discharge begins the apparatus is filled with a gas at a suitable pressure, and the tap turned so as to cut off the connexion between A and B. Then when the currents are sent through the solenoids discharges pass through both tubes, but while the discharge in B continues indefinitely, that in A soon stops. If after this has occurred, and while the discharge is passing through B, the tap is turned so as to open the communication, the first effect is that the dis-

charge recommences in A. (The two solenoids are in series, so that an alternating current is passing through the solenoid round A.) If the tap is turned again so as to cut off the connexion between the tubes the discharge immediately stops. It will start again immediately if the tap between the two tubes is opened. The starting of the discharge in A is not due to electrons passing from B to A, for it occurs with undiminished intensity if a strong electromagnet is placed under the tube connecting A and B. This would prevent any electrons passing from one tube to the other. When the tap is open a faint luminous discharge can be seen passing from B through the piece of quill tubing and the tap. If the tap is kept open the discharge in A soon stops and that in B diminishes and after some little time stops, so that no discharge passes through either tube. If now the tap is turned so as to cut off the connexion between the tubes the discharge in B will slowly re-establish itself, and finally be as bright as it was originally. The spectrum, however, shows lines due to sulphur, so that some vapour of sulphur has leaked into this tube from A. The bulb A remains persistently dark, and no discharge passes through it, even after its temperature falls to that of the room. When the discharge passes through A the parts near the solenoid get appreciably warm, and some sulphur distils from the glass rod on to the walls of the tube.

If, after the discharge has stopped in A, a small quantity of fresh gas is let into this tube, the discharge starts again, though it only lasts for a short time. Anything that produces a current of gas in the tube seems to lead to a temporary revival of the discharge. When the gas in the tube is hydrogen the admission of fresh gas shows some interesting effects. When first the gas is admitted, the discharge in A shows the brilliant red cones characteristic of hydrogen emitting the Balmer lines, the red only persists however for a few seconds, the cones become white and the Balmer lines feeble, and after a short time the discharge stops. If the tap between A and B is open the discharge in B also shows the red cones when fresh hydrogen is admitted, but these persist much longer than in A and are visible after all discharge in A has stopped. The cones in B, however, gradually lose their red colour, become white, and ultimately, as was stated before, the discharge in B also stops provided the tap is kept open. If the tap is turned after the discharge in B has lost its redness but before it has ceased, the brightness of the discharge in B will increase but the red cones will not reappear.

I have tested the effect of different substances on the discharge by depositing a thin layer of the substance of about the same length as the solenoid at the middle of a thin glass rod placed along the axis of the discharge-tube. I have used, in addition to sulphur, silver, platinum, cadmium, the filament of an incandescent mantle, graphite, and found with all these that it was possible to get the discharge bright when the solenoid was not over the covered portion and to cease when it came over it; the effect was very distinctly less marked with the graphite than with the other substances—it required careful adjustment of the pressure to get it at all, and even then it was not nearly so well marked as for the other substances.

The effect is most marked when the pressure is only a few hundredths of a millimetre and gets much less at considerably higher pressures; it does not seem to depend upon the nature of the gas, as I have obtained it in air, hydrogen, oxygen, and helium. If, after the discharge has been running for some time, the tube is strongly heated in the neighbourhood of the place where the substance is deposited on the glass rod, it often happens that immediately after the heating the discharge will pass when the solenoid is over the patch of substance, the place where it was stopped before the heating, but that it is now stopped at some other part of the tube where it went before. This looks as if the effect is due to a deposit of something on the walls of the tube which is driven off at a high temperature. In a short time, however, the discharge stops again when the solenoid is over the patch.

Quite recently I have found that when patches of fused salts, such as potash, soda, sodium chloride, lithium chloride, are placed on the glass rod, the discharge at low pressure goes more easily when the solenoid is over the patch of salt than when it is in the other parts of the tube: this effect is opposite in sign to that produced by patches of metal or sulphur.

Theory of the Effects of Foreign Bodies on the Discharge.

The following considerations may help us to understand the influence of foreign bodies on the discharge:—In order that the discharge should occur the gas has to be ionized. For this energy is required; this comes from electrified bodies which have acquired high velocities under electric force. To start the discharge there must be some electrified bodies to begin with. In a gas in which there was nothing

but neutral molecules it would be impossible to produce a discharge unless the electric field was so intense that it was able to tear the electrons out of the molecule. To do this the field would have to be so strong that the fall of potential in a length equal to the diameter of a molecule is not less than the ionizing potential of the molecule; this requires a field where there is a fall of about 12 volts in 10^{-8} cm., or 1.2×10^9 volts per cm. This is quite a different order of intensity from that in discharge-tubes. It is to stray electrified atoms or electrons, and to stray electrons in particular, that we must look for the initiation of the discharge. Under normal conditions there is always a certain amount of ionization going on in a gas apart from that due to the action of the electric field or visible radiation. This residual ionization, as it is called, gives rise to some 10 or 12 pairs of ions per second per cubic centimetre of gas at atmospheric pressure. This ionization in its initial stage gives rise to free electrons. Before these electrons can ionize the gas, a time must elapse which must be very large compared with the interval between one collision of the electron with a molecule of the gas and the next. For before the electron can ionize it has to get from the electric field energy greater than the ionizing potential of the gas, and it has to convey this energy to an electron in a molecule before that electron can be liberated. When the electric field is not much more intense than the limit which will produce discharge, it may be only one out of a very large number of collisions which will result in the transfer of a sufficient amount of energy. Thus, anything which reduces the life of the electron below the time necessary for it to make these collisions will diminish its efficiency as an ionizer. The electron loses its power of ionization when it unites with a molecule to form a negative ion. In many gases we know from the experiments of Loeb that an electron makes a very large number of collisions before it gets linked up with a molecule, and this number varies greatly with the nature of the gas; thus it is certainly many millions if it is not infinite for pure nitrogen or helium; for oxygen, in which the electron has a comparatively short life, the number of collisions is about 30,000, while in chlorine the number is less than 300. Thus for the electronegative gases this number is exceptionally small. Now, sulphur is a very strongly electronegative element, and presumably a sulphur molecule would be very likely to capture an electron striking against it. If every collision of a sulphur molecule with an electron resulted in the capture of the electron, then even if the partial pressure

of the sulphur molecules was only $1/30,000$ of that of the molecules of oxygen the presence of the sulphur would halve the free life of the electron; if the gas were hydrogen or nitrogen instead of oxygen it would reduce it very much more. Though the vapour pressure of sulphur is exceedingly small, being only $\cdot 0003$ mm. of Hg at 50°C ., it is more than $1/30,000$ of the pressure in the experiments we have described. It must be remembered, too, that when the discharge passes the temperature and therefore the vapour pressure of the sulphur increase. As a matter of fact, we find that there is a deposit of sulphur on the walls of the tube after the electrodeless discharge has been going for some time. It is thus, I think, probable that there may be enough sulphur vapour present in the discharge-tube to curtail seriously the life of the electron and thus diminish its ionizing power and thereby increase the difficulty of producing the discharge.

The experiments described on p. 1153 show that when the tube contains nitrogen, hydrogen, or air, these gases combine with the sulphur, if the compounds so formed are gaseous, or even though they are solids or liquids; if they are more volatile than sulphur they may produce effects which persist after the discharge has stopped if they, like sulphur, possess the power of capturing electrons. This would explain the effects observed with nitrogen, hydrogen, and air where, after the discharge has been passing for some time, the bulb gets into a state when the discharge stops and cannot be started again until a considerable time has elapsed or the bulb been washed out with fresh gas. In helium, where no combination occurs, this permanent effect is not produced; the sulphur diminishes the discharge for the time being, but does not lead to a state in which for some time it is impossible to get a discharge through the tube.

Anything that shortens the life of the electron will increase the difficulty of getting the self-sustained discharge; on the other hand, anything that reduces the number of collisions required by one electron to detach another from a molecule will facilitate the discharge. Thus, if the discharge produces complexes formed by the aggregation of several molecules, it may well be that an electron striking against one of these is more likely to detach an electron than if it struck against a single molecule; thus the presence of such aggregates would facilitate the discharge. We saw that with the apparatus shown in fig. 10, after the discharge had stopped in A and was passing in B, opening the tap between A and B caused the discharge to start in A and

persist for a short time, even though electrons were prevented by a strong magnetic field from passing from B to A. This suggests that aggregates, or agencies which have the power of producing aggregates or which give out radiations which ionize the gas, pass from B to A and help the electric field produced by the solenoid round A to ionize the gas. I found, in the earlier experiments referred to at the beginning of this paper, great difficulty in getting the electrodeless discharge to start in gases which had been very carefully dried; this is intelligible if we suppose that traces of moisture facilitate the formation of aggregates, the moisture acting as a catalyst for the electric discharge as it does in many cases of chemical combination. If this view is correct, the passage of the discharge may be made more difficult by agencies which remove from the gas certain products of the discharge. The discharge, besides producing chemical decompositions and combinations which are permanent, produces other modifications of the gas which only persist for a short time. In some cases, *e.g.* nitrogen or oxygen, the existence of these is shown by after-glows, which may persist for several seconds after the discharge stopped. In other gases the duration of their products is too short for them to produce visible after-glows, but their existence may be inferred from the changes which occur in the properties of the gas through which the discharge has passed. If the E.M.F. round the circuit in the electrodeless discharge is increased from zero to a high value and then diminished again to zero, the E.M.F. when the discharge first begins is nearly always considerably greater than that at which the discharge stops. It does not require as large an E.M.F. to maintain the discharge as to start it. The simplest explanation is that the discharge produces systems which are more easily ionized than the normal molecules. The experiment (fig. 11) supports this explanation strongly, for it shows that an E.M.F. which cannot produce discharge in a normal gas may do so if that gas is put into connexion with a gas through which a discharge is passing. If any substance which has a strong affinity for these easily ionized molecules is introduced into the gas it will remove them from the gas as fast as they are formed, and thus make the passage of the discharge more difficult. The presence of certain metals destroys the after-glow in gases which in their absence give intense glows. The metals destroy the compounds which produce the glows; these compounds are quite probably analogous to the easily ionized ones produced by the discharge—if the metals destroy these

as they do the glow-forming compounds their presence will make the discharge more difficult. The experiments already described show that the presence of metals may retard the discharge and that some metals are more effective than others.

The electrodeless discharge offers great advantages for the study of the effect of impurities on the passage of electricity through gases, for it starts close to the surface of the glass, which is where the impurities might be expected to congregate.

It might seem remarkable that a metal so little volatile as platinum should give off vapour able to affect the discharge.

Lenard (*Wied. Ann.* xxxvii. p. 443, 1889) and Rubens and Ladenburg (*Ber. Deutsch. Phys. Gesell.* ix. p. 749, 1907) have brought forward evidence that under the action of ultra-violet light many substances, including gold, evaporate. Since the electrodeless discharge produces very intense radiation of a very absorbable kind, we might expect that it would make the substances exposed to it evaporate. Again, the "sputtering" of the metal from the cathode in ordinary discharge-tubes shows that under certain conditions metals evaporate at temperatures much below that at which they give out visible radiation.

This may be the explanation of an effect I observed when studying the photoelectric emission produced by the radiation inside the discharge-tube. I found (*Phil. Mag.* ii. p. 687, 1926) that when a metal plate was exposed to the radiation there was, as might be expected, a large leak of negative electricity from the plate. What was remarkable, however, was that when the plate was strongly electrified positively there was a small leak of positive electricity from the plate. It was shown that this was not due to the ionization of the gas around the plate or to the incidence of radiation reflected from the plate on to neighbouring conductors, causing them to emit electrons which found their way to the plate and produced the effect of a leak from it of positive electricity. I have not, however, succeeded in getting direct evidence of the evaporation of thin films of gold exposed to these radiations.

The electrodeless discharge supplies, I think, a convenient method for investigating the effects of various physical agents on the ionizing potential of a gas, and whether or not these produce in the gas molecules more easily ionized than the normal ones; for, as the preceding experiments show, this discharge is very sensitive to anything which alters the ease with which a gas can be ionized.

I have much pleasure in thanking my assistant, Mr. Everett, for the help he has given me in this investigation.

CII. *The Analysis of the Copper Spectrum.*
By W. M. HICKS, F.R.S.*

II. COMPLEX SEPARATIONS AND QUARTET RELATIONS.

Summary.

THE paper begins with a short discussion of the inverse D lines, the result of which is to indicate the possibility that these and 5105, with the separation 2042, may not belong to doublet systems as generally supposed. Evidence is given for the existence of quartet systems depending on d terms with separations 2042, 1412, 894, and with separations completely following Landé's separation rules. Several other quartet examples are given, but no general discussion of the whole spectrum on this basis is attempted. Shenstone's lists of fundamental lines with 2042 separations are then discussed. An attempt is made to allocate them on the basis of the maps of [I] and to test these allocations by quartet arrangements and summation sets. In spite of the appearance of perfect quartet sets in which the separations follow Landé's rules, the evidence seems to lead to a suspicion that the 2042, 1412, 894 are composite, depending on association of links and term displacements. The quartic arrangements given by Beals, adopted later by Shenstone and by Sommer, are then specially considered and certain difficulties connected with their two-term theory of line constitution discussed. The evidence from the Zeeman effect appears on the whole to contradict the allocations suggested by them, but the conclusion is drawn that Landé's rules for Zeeman patterns do not apply to these systems. The majority of their quartet separations appear also to be composite, and the quartets involved are not real ones. It would appear, however, that as many new questions arise as are definitely settled.

The present paper is a sequel to that on the "Analysis of the Copper Spectrum" appearing in vol. ii. p. 194 of this journal †—referred to here as [I.]. It deals chiefly with the question of multiplicity in the spectrum of this element. It had been intended to begin with a consideration of the collaterals of the ordinary S, D series ‡ lines and a more complete discussion of the F and various P series. These are specially interesting, as collaterals enter in

* Communicated by the Author.

† The reader must be acquainted with the results of this paper, and especially must have its maps and Table A at disposal for continual reference. References to papers are given in three sets of numbers, of which the first gives the volume, the second the page, and the third the last two digits of the year, thus 12 means 1912, but a year of the previous century would be given in full.

‡ Shenstone, *Phys. Rev.* 28, 462, 26, appears not to have known that these series had already been allocated up to $m=10$. (*Phil. Mag.* 39, 457, 20, referred to later as [A] and 'Analysis of Spectra' (1922), p. 252.).

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considerable numbers concurrently with a sudden diminution of intensity and change of character at S (4), D (4). Thus for successive orders $m=2, 3, 4$ the intensities of S₁ are 10, SR, 2n and of D₁₁ are 10 R, 10, 2n. The length to which the quartic discussion has extended has, however, compelled me reluctantly to exclude this portion.

The "Inverse D" Lines.

1. **T**HE sets of line pairs with the doublet separation which occur in analogous positions in the elements of this group, were allocated by Runge and Paschen as inverse doublet D sets, without D₁₁ representatives, since their Zeeman patterns as determined for Cu* and Au† seemed, with the knowledge of the Zeeman effect at that date, to point to corresponding D relations. Corresponding D₁₁ lines were later suggested by me [A. p. 469]. The great advance in our knowledge since then, due to Landé, calls for a re-discussion and re-statement, especially as the allocation of the D₁₁ does not seem to have met with general acceptance. Their appearance in the spectrum of each element gives opportunity for a comparative discussion. The following table gives a conspectus of their appearance to different observers and under different conditions:—

	Copper.										Silver.				Gold.					
	K.R.	A.	A.s.	H.a.	H.s.	E.V.a.	E.V.s.	E.H.a.	E.H.s.		K.R.	K. ⁽¹⁾	W.	E.V.s.	K.R.	E.H.a.	E.H.s.	E.a.	E.s.	E.V.s.
D ₂₂	8	6r	6	8	10	8	8	50	10r		4r	ft.	3	1?	4	4	1	4	6	3
D ₁₁	1n	1		1n	1n	3	1n	1	1		2r	2r	-	-	4	2	2	1n	5	8
D ₁₂	8	5	4	6	8	8	6	8	8		1r	1	-	-	2	2	1	2n	2	2

(¹) Remeasured from K.R.'s old plates.

Here K.R. denotes Kayser and Runge. A., Aretz. H., Hasbach. E.V., Eder and Valenta. E., Eder. E.H., Exner and Haschek. K., Kaspar. W., Walters. a=arc. s=spark. These initials are used throughout this paper.

The only normal march of intensities is that given in Au by E.V. in the spark or K.R. in the arc. The outstanding facts are:—

(1) The apparent reversal of the order of intensities in the D₁₁, D₁₂.

(2) Their independence of arc or spark conditions except in Au, where the spark enhances them.

* Hartmann, *Ann. d. Phys.* 38, 43, 12. Runge and Paschen, *Berl. Sitz.* (1902) p. 720.

† Hartmann, *loc. cit.* Purvis, *Proc. Cam. Phil. Soc.* 14, 217, 07.

(3) The extreme faintness of the whole set in Ag (only observed by K.R.) and their considerable intensity in Au. The relation of this to the abnormal double valency of Cu, the normal valency of Ag, and the abnormal of Au, strikes the eye at once, suggesting connexion of these sets with the additional electrons transferred from the core.

It might be objected that the allocation of D_{11} in Cu is not correct, but this is met by the facts that in Cu and Ag the separations exactly fulfil the own conditions, the D_{11} in Cu comes essentially into the relations of map V., starting with the Y_2 link, whilst a reference to [I. pp. 207, 208] shows that, in Ag, D_{11} has the Y_1 link back, and, in Au, the X_1 forward, and finally the fact that in Au the observed Zeeman pattern fits the D_{11} allocation. As possible explanations may be suggested:—

(1) The D_{11} has been disrupted almost wholly into other collaterals.

(2) A normal D set has been displaced or linked so that, while the normal $p_1 d_1$ transitions have nearly all taken place and a few displaced (obs. D_{11}), the majority of the $p_1 d_2$, $p_2 d_2$ have been displaced to the set in question, and a few only or none of the normal transitions have occurred (see example below). Indeed, the spark nature of the set suggests displacement or linkage.

(3) In Cu the D_{11} line belongs to the system of the faint companions of the known complex lines D_{12} , D_{22} , and the main lines are an independent type.

In connexion with his research on the ultra-red spectrum of Cu, Randall * denoted by x (later by me d_2') the unknown term combining with p_1 , p_2 to give the doublet, and at the same time allocated lines to combinations with it, of $f(3)$, $f(4)$, $d_1(2)$, $p_1(2)$, $p_2(2)$ of which, however, that with $d_1(2)$ cannot be sustained, nor can one at least of the last two.

2. Shenstone has adopted a suggestion by Ruark and taken in Cu the strong line 5105·543 (F.B.), $n=19581\cdot115$ as the corresponding D_{11} . If it be written $y-p_1$, the value of y , since $p_1=31524\cdot53$ is 51105·65. He has given a long list of combinations of this y and x with several other terms, which he has arranged in sets in the form

$$s-q_1, \quad x-q_1, \quad y-q_1,$$

$$s-q_2, \quad x-q_2.$$

These have formed the starting-point for quartet allocations

* *Ann. d. Phys.* 33, 739, 10.

by himself and by others. It must be admitted that as they stand, *i.e.*, if q_1, q_2 are *related* terms, the selection rules require j values of 2, 1 for q_1, q_2 (*i.e.*, p terms) and 3, 2 for y, x , or y is a real d_1^2 term. But there is nothing to show *à priori* that a particular pair chosen is to be taken as related. If, however, the connexion of q_1, q_2 be allowed it follows that y must be a d_1^2 or 233 term. Other evidence, however, seems to be definitely against y being the d_1^2 of the inverse set, quite apart from the reasons given above, that they already possess a different d_1^2 term of their own.

(1) In all the immense number of known cases, the satellite separation is a small fraction of the doublet separation. Here it is $2042/248 = 8.2$ times larger.

(2) In only a few cases do we find the satellite term less than that of the main lines. Here it is 49062 as against 51105.

(3) The satellite separation of a doublet depends exactly on our displacements in all known definite cases. Here the separation is 2042.876 (error certainly $< .01$). We have then

$$\begin{array}{ccc} 49062.77 & 2042.88 & 51105.65 \\ R/(1.495151)^2 & 30188 & R/(1.464963)^2 \end{array}$$

The displacement $30188 = 4\Delta + 26\delta_1 + 10.5$.

The 30188 is correct within unity in the last significant figure, and the greatest possible error in $4\Delta + 26\delta_1$ does not exceed .5. Thus the displacement definitely cannot be an our multiple. The result is fatal against 51105, 49062 being d_1^2, d_2^2 terms of the *same* system. This argument holds only if the d are to be doublet terms. If the multiplicity is higher than 2, we may expect from analogy something similar to the well-established triplet modification, where the our rule never applies exactly to each of the separations, but is absolute for their sum.

(4) In the red region King finds 5105 the only line seen in the furnace spectrum, whereas the two D_1' 5782, 5700, should also have been visible if they also were furnace lines. This we should expect if they belonged to the same system. It may be noted that 5105 is a single line of "great sharpness" (Janicki) whereas the other two are complex.

(5) To compare the respective effects of the arc and spark excitations we may take the observations of Hasbach.

	arc.	spark.
$x - p_2$	8	10
$x - p_1$	6	8
5105	8n	4

This clearly shows a remarkable difference in their reactions

to arc and spark. Whereas 5105 behaves as if it were a normal series line, the other two behave as if they were linked lines, *i. e.*, enhanced by the spark. Indeed, here the separation 2042·88 suggests at once a $3u$ link = 2041·89, with a displacement on the x or y term. If such displacement occurs in x the own shift is 2·40, if in y it is 2·55. If we take the Rydberg $u' = 680·11$, $3u' + (-\delta_1)$ on $x = 2040·33 + 2·40 = 2042·73$ and $3u' + (-\delta_1)$ on $y = 2042·88$. As these numbers are all accurate to the last decimal, the latter, which reproduces the exact separation, must, if this linkage relation be real, be taken, and the former cannot be admitted. It would mean, a case already suggested, a possible normal inverse D set with a satellite separation 2·55, inverted as in the F series, in which the D_{12} , D_{22} lines in the actual excitation are shifted by $-3u'$. Thus for illustration

5782	17289·80	$3u'$	(19330·13)	} 2·55	248·44
5105			19581·12		
5700	17538·24	$3u'$	(19578·57)		

the lines in brackets denoting the supposed normal unlinked D_{22} , D_{12} . Against an explanation of this kind may be placed the fact that, as a rule, linkage separations are very frequently accompanied by term displacements, which vary with the terms involved, whilst in the seven examples given by Shenstone with reliable readings, all the separations involved agree within ·01 of their mean. On the other hand, we do find a very considerable number of $3u$ linking, *e. g.*, amongst others,

1. (8 vi) 27664·185 **2041·877** 29706·062 exact $3u$.
2. (3 vi) 27401·610 **2040·92** (31 vi) 29442·534 with complete chain, viz.
(3 vi) $+M+X+e+L+u+u-L-M-e-X+u$ (31 vi) $=3u$.
3. 1n, 3883·73; 25744·29 **2040·96** 27785·25 $S_1(5)$.

This, as attached to $S_1(5)$, can have no relation to the y x separations here considered. It is $2u' + u = 2040·85$ within O.E. of either line

$$\begin{aligned} \text{E.H. } \left\{ \begin{array}{l} 20128·41 \quad 3 \times 680·46 \quad 22169·77 \quad (8 \text{ viii}) \\ 29·46 \quad 3 \times 680·10. \end{array} \right. \\ 5. \quad 24973·92 \quad 3 \times 680·52 \quad 27015·48 \quad 3 \times 680·53 \quad 29057·08 \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (22, 18, 19 \text{ xiii}). \end{aligned}$$

Another possible allocation for the 5105 must not be passed over without notice. As a fact numerically it is $D_{11}^2(2) \cdot Y_1 \cdot Y_2$. Both lines have been measured by interferometer methods by Fabry and Buisson to three places of decimals (say possible O.E. $d\lambda = \cdot 002$, $dn = \cdot 005$). They give $19581·115 - 19158·370 = 422·745 \pm \cdot 01$; whilst $Y_1 + Y_2 = 210·21 + 212·54 = 422·75$. The agreement is exact, and it

appeals to me as very strong evidence for the reality of the relation indicated. The two suppositions, however, correspond to essentially different constitutions. In this, p_1 enters as a positive term, in the former, as negative. Nevertheless, in the present paper I have discussed the data on the basis of the assumption made by Ruark, Shenstone, Beals, and Sommer, *i. e.*, as $y - p_1$.

The Evidence from the Zeeman Effect.

3. Let us now see what information the Z.P. can offer as to the term-types of these three lines, in view of the new knowledge since 1920 given by Landé's rules. The theoretical patterns involved for the D^2 , D^4 lines are as follows, the displacements being given as ratios to the standard shift. The strongest components in ϖ , σ and the smallest ϖ only are entered, other components being indicated by dashes. The intervals between components are twice the smallest ϖ . The first two figures in each case give the j values for the p , d terms respectively.

1, 2 D_{22}^2	·07/-, ·87	2, 2 D_{12}^2	·80, ·27/-, 1·07, -
2, 3 D_{22}^4	-, ·18/·83, ---	3, 3 D_{12}^4	·57, -, ·11/- - 1·49 - -
	2, 3 D_{11}^2	- , ·07/1·00 - - -	
	3, 4 D_{11}^4	- -, ·09/1·00, - - - - -	

$-D_{22}'$, $\lambda=5782$ was examined by Hartmann and by Runge and Paschen. Both give 0·83, but Hartmann also states "further decomposition into 6 or 9 components possible." Omitting F and higher order lines the only types capable of giving this not fully resolved pattern are D_{22}^2 and D_{22}^4 , either of which is capable of producing a merge 0·83, but D_{22}^2 has at most only six components, and the separation of the components ($\cdot13$ or $d\lambda=\cdot03$) is too small to have allowed them to be seen as separate by Hartmann. On the contrary D_{22}^4 has the exact $\cdot83$, and the component separation ($\cdot36$, $d\lambda=\cdot1$) is large enough to have enabled the separate components to have been recognised as such.

$-D_{12}'$, $\lambda=5700$. Hartmann shows "a quite complicated decomposition. Under specially favourable conditions only four parallel could be certainly established of which the outer pair showed three times the intensity of the inner. With the four parallel, twelve components on the whole were ordinarily to be concluded." Runge and Paschen found the D_{12}^2 pattern without the internal ϖ pair, not to be unexpected perhaps in view of Back's * more recent observations that the corresponding components in the D_{12}^2 lines in Th, Ba, Cu are extremely faint. The eight σ of Hartmann cannot possibly be met by the doublet type, and it would

* *Ann. d. Phys.* 70, 333, 23.

seem that the lines observed by him were of quartic type. This carries with it the necessity that in these lines at least the p terms are also quartic, for their j values must be 3, 2 and they cannot be intercombination. In the case of Au, Hartmann gives for $-D_{22}'$, 0.885, none for $-D_{12}'$ and 0.111 for $-D_{11}$. These are not decisive as between doublet and quartet.

$\lambda = 5105$. Hartmann gives 0.110 and recently Sommer 0.110. It is noticeable that these agree with that for AuD_{11}' . The strongest σ should be 1.00 in both doublet and quartet types, but as Back (*l. c.*) finds intensity ratios 9 : 7 : 3 : 1 and the components are only separated by about .18 in either case, a merge at 1.11 is to be expected. There are, however, other observations which fit the observed more exactly ; in fact, $f_1^2 f_1^2$ ($j=4$) requires 0.114, or $g_1^2 g_1^2$ ($j=5$) 0.111. In any case, even if y is a d_1 term, there is nothing to decide whether it is doublet or quartet. One apparent way to avoid the quartet decision is to suppose that the extra components are caused by the complex nature of the inverse D lines. Their companions, however, are so faint, compared with the main lines, that any effect due to them would be too weak to affect the observations. But another supposition, however upsetting according to our present ideas, might be mentioned, viz., that the doublet and quartic term values for $m=1$ are practically the same, and that the observed multiplicity depends on the excitation. On this basis the complex nature of these lines would be explicable, the main belonging to the doublet and the weak to the quartet or *vice versa*. In this connexion see the discussion as to the nature of $s-p_a$ in § 6, p. 1173.

However, let us accept for a moment the quartet allocation, and see to what it leads. The j for d^4 are 4, 3, 2, 1. Hence we should expect separations in the ratio 7 : 5 : 3 with the first = 2042. The other two should then be about 1450, 875. The j for p^4 are 3, 2, 1 requiring separations in the ratios 5 : 3 with the first = 248, so that the next should be about 150. A search gives at once the following quartet :—

4	3	2	1	
		2rv, 15723.63	894.05	6, 14829.58
		153.57		153.77
	6rv, 17289.797	1412.60	2, 15877.20	893.85
	248.44	249.46	5rv, 14983.35	
3, 19581.115	2042.88	5, 17538.238	1411.58	1, 16126.66 ⁽¹⁾

(¹) By Aretz, who gives no rv notation.

Moreover, the P doublet is completed thus:

1) 10, 30783.592 248.375 $P_2(1)$ 10, 30535.217 153.876 $P_3(1)$ 4, 30381.341

As they stand, these form a perfect fourfold triplet and quartet—order of intensities, of separations and characters. Nevertheless, the $P_2(1)$ has been quite definitely shown by Purvis* to be of doublet type. The P_1^2, P_1^4 might possibly not be distinguished, with Z.P. = $\cdot 33/1\cdot 00$ — and —, $\cdot 20/1\cdot 00$ — — —, but there can be no question as between P_2^2, P_2^4 with Z.P. = $\cdot 67/1\cdot 33$ and $\cdot 40$ — — $1\cdot 87$ —. How is the difficulty to be met? Possibly the explanation is that the “ d ” separations are mixtures of links and displacements, whilst the p sep. = 153 depends on the $-3b$ displacement on p_2^2 . We have already seen how 2042·88 can be explained by the $3u'$ link and $d_2 = d_1(\delta_1)$. Also $3u - 3X_1 = 1412\cdot 25$ and $u + Y_2 = 893\cdot 17$ with small displacements might meet the 1412 and 894 separations. The three d separations above occur, as will be seen later, so frequently and in multiplet association, that the conclusion seems forced on us that these multiplets are not pure, *i. e.*, depend on displacements only, but are compounds of links and displacements. We shall see below that the same phenomena appear in the quartets which have been proposed by several recent writers. If so we are met with the problem as to the effect of displacement and linkage on Zeeman patterns. Displacement produces new terms and a change in the Z.P. may be expected, not subject to Landé's rules unless such new term is a normal one (*e. g.*, in the above instance where a d_2 term is produced by one own displacement in a d_1). In the case of linkage further experiment is required to show whether any change is produced or if so what. In the above example, $3u$ —or $Y_1 + Y_2$ on D_{11} on alternative supposition—seems to have produced no change †. On the other hand, we find examples of such change, *e. g.*, the two lines (1 n) 46173·55, (6R) 44173·68 linked by $1999\cdot 87 = 2e + \cdot 27$ ($d\lambda = \cdot 01$) have quite different Z.P., viz. $\cdot 45/66$ (Shenstone) and $0/79$ (Sommer). It would be instructive also to learn whether the Z.P. of a summation line is to be obtained from Landé's rules by adding the term components instead of subtracting. It would mean very greatly increased spreads in the patterns observed, so that even weak fields would resolve them. Unfortunately, summation lines must, as a rule, by the nature of the case, lie in the ultra-violet, and they are generally of small intensity.

* Proc. Camb. Phil. Soc. 14, 225, 07.

† We have a similar result in a pp' multiplet in Ba which is bodily linked by e to its normal position, membra disjecta of this latter being also in evidence. Here also the Z.P. of all the lines remain the $0/3/2$ for this type. See ‘Analysis,’ pp. 223, 278.

The Shenstone Lines.

5. The further consideration of multiplet systems on the basis of the quartet (A) above must involve a discussion of the list of lines with separations 2042, 13245, which we shall denote by ϕ , θ , given by Shenstone* in his first paper. Those writers—Beals†, Sommer‡, Shenstone* himself—who have used the latter's list as a starting-point for the allocation of multiplets, have accepted the doublet d type for the y , x terms, and naturally have taken this to hold for the corresponding sets in his list. For some of these we have data as to their Z.P. by one or other of these authors. We shall postpone consideration of further multiplets until these magnetic data and the constitution of these lines have been discussed. The lines are reproduced as to their wave numbers in table i. together with other information as explained at the foot. It is followed by table ii. containing a list of some other lines and sets involving the same separations and which we shall require later.

TABLE I.

		s	13240+	x	2042+	y
221	$P_2(1)$	10R, 30535·217	5·420	8, 17289·797		
248		Z. A. D. E. K. i. $a^{(1)}$		Z.		
222	$P_1(1)$	10R, 30783·592	5·354	6, 17338·238	·862	8n, 19581·100
		Z. A. D. E. K. i. $a^{(2)}$		Z.		
422	p_a	8, 40114·024	5·487	2, 26868·537	·868	3, 28911·405
829		Z. A. B. ii.		(38 vi) S'.		Z. S'.
421	p_b	6, 40943·241 ⁽⁶⁾	4·909	2, 27698·332		
		Z. A. B. iii.		Z.		
432	p_c	2, 44544·659	5·982	6, 31298·677	·931	2, 33341·608
371		Z. B. C. i. a		Z. C. S. (17 ii)		Z. C. S'.
431 ⁵	p_d	2R, 44916·378	6·094	3, 31670·284		
		Z. A. B. E. i.		Z. C. S' (23 ii)		
221	p_e	1n, 45821·84	6·44	2, 32575·399		
58		Z. A. E. i.		(16 iii)		
222 ⁶	p_f	1n, 45880·08	6·24	6, 32633·841	·859	4, 34676·700
		Z. A. C. i.		Z. A. S. (30 ii)		Z. A. S.
232 ⁷	p_g	1n, 46173·55	6·17	6, 32937·382	·851	3, 34970·233
3209		Z. A. B. E. i.		Z. A. S. (3 iii)		S'.
222	p_h	4n, 49383·07	5·50	8, 36137·572	·582	10R, 38180·15
		C. E.		A. (1 ix)		Z. A. iii. (2 ix)

* Phil. Mag. 49, 952, 25. Phys. Rev. 28, 449, 26.

† Proc. Roy. Soc. 111, 168, 26.

‡ Zeits. f. Phys. 39, 711, 26.

TABLE I. (*continued*).

	<i>s</i>	13240 +	<i>x</i>	2042 +	<i>y</i>
243 A			3, 30480·697	·872	4, 32523·569
680·10			Z. S. (6 i)		Z. C. S. (5 iii)
433 B			4, 31160·804	·873	5, 33203·677
			Z. C. S. (5 i)		Z. A. S'. (7 iii)
233 ^a E			4, 33352·963	·709	8, 35395·672
			Z. C. S. (13 <i>a</i> iii)		Z. A. v. S'.
F			6, 41538·701	1·02	8R, 43581·72
					C. ii.
Q	1, 55028·5	6·2	2R, 41782·287	1·23	2, 43825·52
			O.		
M	2, 56358·9	20·6	4, 43098·34	·67	6R, 45141·014 ⁽³⁾
	5, 13206·25 (·02)	(29892·09)	9·62 (·37)		C. i. K.
				[13249·79	4 <i>n</i> , 29848·55]
K	6, 57426·38	12·70	6R, 44173·68		
iv 2	1 <i>n</i> , 14281·74 (·10)	(... 91·94)	·47 (·4) Z. C. i. _a	[13234·03	4, 30939·65]
J	3, 57942·7	(-1·7)	1 <i>n</i> , 44704·40	·74	1 <i>n</i> , 46747·14 ⁽⁴⁾
^a iv 49	2 <i>b</i> , 14812·29 (·10)	(... 92·11)	3·20 (·30) C. v.		O.
				[13249·22	1, 31455·18]
233 ¹⁰ N			6R, 44874·55	1·51	1, 46918·062
	3, 14983·36 (·02)	(... 91·19)	3·94 (·20) Z. C. i. K.		K.
				[13238·58	2, 31635·97]
221 ¹¹ R			4R, 45119·39	(-2·11)	0, 47159·28 ⁽⁵⁾
iv 5	3 <i>n</i> , 15226·841 (·07)	(... 92·55)	Z. C. i. K.		

The columns under *s*, *x*, *y* give the wave numbers; the second gives Shenstone's notation for the supposed second term, and the first the quantum numbers adopted by him in the order *rkj*, the fourth and fifth give the separations as additional to those entered at the top. The letters underneath have the following meanings:—Z. the Z. P. has been observed, S. denotes a satelloid, S'. one observed as such by Stücklen; A., B., C. denote Shenstone's classes, A. excited by bombardment, B. absorbed by vapour, C. excited by arc of 8 volts and *not* A.; E. absorbed by vapour, Zumstein (Phys. Rev. 25, 523, 25), K. Do. Kichlu (*Zeits. f. Pys.* 39, 572, 26); i. ii. . . v. Stücklen's classes of absorption in underwater spark.

(¹) Absorbed by vapour above 1080°. (²) Do. above 1050°, Grotian.

(³) By Wolfsohn, *Ann. d. P.* 80, 415, 26. (⁴) Dreblow. H. gives 46748·26 or

(⁵) Pina de Rubies. 2*y* larger.

Other allocations 5, 232—6, 232—7, 432—8, 433, all by B.

9, 221—10, 243—11, 232, all by S.

The numbers in [] have been added for later reference.

It should be noted that whilst in the first sets down to A (*p_h* excepted) the ϕ are equal, the θ vary outside O.E., but it is remarkable that the variations seem to depend on the *y*. Thus, taking $\theta = 13245·40$, the deviations are ·02, -·05, ·09, -*y* + ·08, *y* + ·01, *y* - ·12, 2*y* - ·10, ·84, *y* + ·20, ·10.

TABLE II.

θ , ϕ represent the separations $s - x$, $y - x$, also stand for abbreviations:
thus, θ 5·61 stands for 13245·61; ϕ 4·51 for 2044·51.

1.	{			2, 11836·11 (7 iv)				
				247·42				
		1, 25329·27	θ 5·64	1, 12083·53 (8 iv)				
2.	1n,	25401·67	θ 4·21	1, 12157·47	ϕ 4·51	3, 14201·98 (39 iv)		
	{	2, 27660·66	θ 6·69	2n, 14413·97 (3 iv)	211·99			
3.			680·06					
		4, 28340·72						
4.	1,	25468·74	θ 5·61	2, 12223·13 (1 iv)				
	{	2n, 26271·71 (53 vi)		6, 14829·58	249·82	1n, 15079·40		
			1000·18				995·1	
		2, 27271·89 (4 vi)	θ 40·00	1, 14031·89 (4 iv)	ϕ 2·6	4n, 16074·5 (s)		
5.	{	249·09		249·85				
		1, 27520·98	θ 39·24	1n, 14281·71 (2 iv)				
		680·01						
		2, 28200·99						
6.	sat.	56·39	θ 6·43	2, 14509·96 (12 iv)	ϕ 2·30	2, 16552·26 (22 iv)		
2·22	6,	2·7754·17 (51 vi.)	θ 6·28	2, 14507·89	246·79	2n, 14754·68 (11 iv)		
				2n, 13897·48				
	{	1, 28552·60	θ 6·26	1408·86				
1·71		1,	28550·89	θ 4·55	1, 15306·34 (9 iv)	$[\phi$ 9·07]	1n, 17355·41 (s, 19 vii)	
7.			241·61		247·35		247·71	
		3,	28792·50 (24 vi)		2, 15553·69	$[\phi$ 9·43]	3, 17603·12 (s, 8 v)	
		Note, 1·71 = 3y probably satelloid.						
	{	1. 3, 29384·15		6. 1n, 18330·93 s		11. 1n, 17704·43		
		2. 2n, 29535·26 (i)		7. 2n, 16537·79		12. 1n, 17706·92		
8.		3. 2, 16293·87 (51 iv)		8. 3, 18580·23 (s 8 vii)		13. 1n, 17712·37 s		
		4. [90·00]		9. 3, 16045·04 (43 iv)		14. 1, 19754·62 s		
		5. 0, 18335·7s		10. 1, 17456·13 (5 v)		15. 1n, ... 59·62		
		See map XI.						
				4n br, 21282·02 (9 viii)				
9.	{			251·60				
		1, 34777·40	θ 3·78	2n br, 21533·62 (11 viii)				
10.	1,	37845·30 s	θ 1·66	4n br, 24603·64 D ₁₂ (3)	ϕ 39·86	2n, 26643·50 s		
				6n br, 07·29 D ₁₁ (3)				
11.	1n,	42302·54 (17 xiii)	θ 5·46	3, 29057·08 ¹ (43·vi)				
12.	1n,	42334·26	θ 3·45	1n, 90·81 (20 vi)				
13.	{	1, 42386·85	θ 46	1n, 68984·07	diff. summation.			
		62308·4 = s(1)						
		(McL) 82230·1						
	{		2n, 16251·51	3·80	1, 16255·31 (45 iv)	ϕ 3·31	4n, 18298·65 s	
14.				243·24	243·29		243·57	
		2n, 16490·99	3·86	2n, 16494·75 (48 iv)	3·85	16498·60	ϕ 3·52	
				6, 21249·87 (sat. 5 viii)			2n, 18542·13 (15 v)	
				248·11, 4·27				
15.	{			97·98				
			1407·91					
		1, 20090·07		8, 21494·15 (sat. 7 viii)	ϕ 34·37	4, 23528·52		
				88·75	ϕ 39·77			

(¹) With two successive — ϕ , see No. 5, p. 1165, and map XIII., 19.

6. The following statement gives the Z.P. according to Landé's rules for the suggested allocations of the terms and those actually observed. B., Sh., S. stand respectively for Beals, Shenstone, and Sommer. The allocations given in the first column are to be supposed combined with $s=211$, $x=232$, $y=233$.

p_a	13/160, 1·86 *		·27, ·80/40, ·93, -- *
422	·39/1·52		B. ·25, 79/33, ·84
	Sh. 0/1·69; S 0/1·80		
p_b	·33/2·33 §	·93/13, 1·73 *	
421	B. 0/2·27; Sh. 0/2·34	B. ·91/0; S. ·97/0	
p_c	·40/80, 160 †	·20, ·60/60, 1·00, 1·40 §	0/1·20 †
432	Sh. ·45/1·66	B. ·39/1·18; S ·44/1·05	Sh. 0/ < 1·7
431	1·00/1·00 †	·40/40, 1·20 †	
p_d	Sh. ·91/1·11	B. ·31/1·10	
B. 232	= ·60/20, 1·40 †	= 0/80 †	
p_e	·67/1·33 †		
221	Sh. ·77/1·21		
222	·33/1·00, 1·67 †	·27, ·80/53, 1·07, 1·60 †	·07, ·20/1·00 --- §
p_f	Sh. ·43/70, 1·5	B. ·50/1·13; S ·52/1·18	B. 0/1·22; S 0/1·16
B. 232		0/80 †	-, ·20/-, -, 1·80 †
232	·60/20, 1·40 †	0/80 †	
p_g	Sh. ·45/66	B. 42/-	
B. 432	= ·40/80, 1·60 †	·20, ·60/20, ·60, 1·00	
p_h			·07, 20/1·00 --- *
222			S 0/1·12
A		·03, ·09/77, -- ·94 †	·17, -- ·86/-- 1·03 -- †
243		B. 0/1·56	B. ·30/1·10; S 64/1·51
B		·29, ·86/-- -- 2·23 †	·09, --, ·43/-- 1·29 -- †
433		B. ·19, ·57/1·67	B. 0/1·19; S 0/1·15
E		·20, ·60/1·00, --, 1·80 *	0/1·20 * §
233		B. ·21, ·68/1·85;	B. 0/1·24; S 0/1·23;
		S 21, ·68/1·85	Sh. 0/1·2
K		·07/73, ·87 §	
221		S 0/79	
Sh. 233		(Sh.) ·20, ·60/1·00 - 1·80 †	
N		S 0/79	
S 243		(S) ·03, 09/77 -- ·94 †	
Sh. 221		(Sh.) ·07/73, ·87 †	
R		S 0/96	
S 232		(S) = 0/80 §	

In discussing these results, unfortunately we cannot proceed with complete certainty, for the lines may belong to

Landé's types of higher degree, or they may be subject to the link and displacement modifications already referred to. Also very few of the observations give fully resolved patterns. We should probably be justified in assuming that Landé's rules either hold or do not hold for all the lines in the same horizontal set, *i.e.*, for combinations of the same term with s , x , y . The observations, however, are not sufficiently exact to enable any reliable determination of the splitting factor to be made.

In the above statement I have attached signs to indicate where, as it seems to me, agreement or otherwise is shown between the allocations and the observed Z.P. * denotes agreement, † definite disagreement, § doubtful. In sp_a there is an unaccountable difference between the observations of B and the others. It is curious that while the others agree with $s^2-p_1^4$, B is compatible with $s^4-p_1^4$, Z.P. = .20, .60/1.00, 1.40, 1.80, 2.20, provided the intensities are not very different. In the case of p_h the observed Z.P. is precisely the same as that of the 5105 or $y-p_1(1)$, which is as it should be, since we know on other evidence that p_h is $p_1(2)$. sp_b has been marked § because the ϖ separation of .67, although large, here corresponds to $d\lambda = .04$, and may possibly be allowed as unresolved 0. yE is marked *§ because there are several cases with Z.P. = 0/1.20, and the observed are closer to others. An examination of the table shows that agreement between the proposed allocations and the corresponding Landé formula fails in the majority of cases. It may be noted that one in nine support $x = 232$, and possibly three in six support or do not exclude $y = 233$.

7. Let us now examine the observed Z.P. and possible allocations on the basis of the Landé formulæ.

p_a, p_b as above with four-fold p .

sp_c is better met by $P_1^4 = .20, 60/1.00 - - 2.20$ †, $x p_c$ by $p_2^4 p_3^4 (j=2, 1) = .47/1.27, 2.20$ †. A very considerable number G^4 fit $y p_c$, *e.g.*, G_{13}^4 or $445-454 = - -.08/ - - - 1.69$ *.

sp_d agrees exactly with G_{23}^4 or $444-454 = .89, - - - / - - - 1.11 - - -$; $x p_d$ none.

sp_e agrees exactly with G_{12}^4 or $445-455 = .73, - - - .08/ - - - - 1.25 - - - -$.

sp_f agrees with $s^2 d_3^4$ or $211-432 = .40/80, 1.60$; $x y_f$ none; $y p_f$ satisfies $d_1^2 d_3^4$ or $211-432 = 0/1.20$.

p_g none.

yp_h may also be D_{11}^4 .

xA. $d_1^4 d_2^4$ or $434-433 = \cdot 03 - - / - - - - - 1\cdot 57$ agrees exactly and gives $x = d_2^4$ and $A = d^4$, or 434 , but then yA as $434-434$ does not give either of the observed patterns. $p_2^2 p_3^4 = \cdot 20, \cdot 60 / - 1\cdot 53 -$ agrees well with S, and d_1^2 / d_3^4 or $233-443 = \cdot 09, \cdot 26, \cdot 43 / - - 1\cdot 11 - -$ with B.

xB. $232-233 = \cdot 20, \cdot 60 / 1\cdot 00, 1\cdot 40, 1\cdot 80$, requiring for yB or $233-233 = 0 / 1\cdot 20$. Both fit, making $B = d_1^2$, $x = d_2^2$, $y = d_1^2$.

xE. This and **xB** agree closely, but definitely differ. They look like modified Landé formulæ. It is remarkable that in **xE** both B and S give exactly the same measures.

xK, also $F_{33}^4 = \cdot 09, \cdot 26 / \cdot 77 - -$, is good—N same as K.

R. There is an extremely large number of combinations which will satisfy the observed $0\cdot 96$ —the best again with F or G, *e. g.*, $G_{22}^2 = \cdot 02 - - / - - - - - \cdot 97$; $g_3^4 g_3^4 = 0\cdot 984$ etc., etc.

Collecting the results, we have

1. Good evidence that $p_a = 422$, whilst $p_b = 421$ is not excluded.
2. No evidence for the constitution of $p_c p_d p_e p_f$, A, E, K, N, R.
3. p_f is 431 with **sxy** two-fold.
4. B is 233 with **xy** two-fold.

Although many of the lines are completely met by F, G combinations, these would be excluded if *s, x, y* are of the nature of *s d d* terms.

The conclusion so far must be, not that the allocations by B. S. Sh. are necessarily wrong, but that Landé's rules do not apply. That consequently the sets are either those of his higher degree or the lines are not simple but involve more than two terms (links or other term differences).

Constitution of the Shenstone lines.

8. We now return to the discussion based on observed inter-relations in the spectrum. We shall begin by an independent discussion of the fundamental sets given by Shenstone in his first paper (table i.). We have already seen in [I.] how a large part of the spectrum is formed of linkages—many of them very long—attached to definite

series lines and involving the well-established e, u, v links with new ones X, Y based on $d(1)$. The maps there given are not, however, exhaustive, and the new Shenstone separations 13245 and 2042 had not then been recognized. Both these separations, or the very closely related ones of $13e + v = 13245.84 \pm .6$ and $3u = 2041.8$, occur also in large numbers throughout the whole spectrum from the ultra-red to the ultra-violet (see table ii. for some examples). There is also an exceedingly large number near the doublet value 248, as indeed Rydberg had noticed, and this is found also in the ultra-red region observed since his time.

The very great equality of all the corresponding separations found in table i. has already been referred to as affording strong evidence, taken alone, in favour of s, x, y being definite terms common to all the sets. But the large number of similar, but not exactly equal, values found throughout the spectrum, some examples of which have been given above, would seem to indicate that they also occur with qualities analogous to those of links. We shall leave the question of their real nature at present open, and simply regard them as constant quantities which, by being added to or deducted from the wave-number of one line, give that of another. It will not then follow that lines separated by these $\theta\phi$ must all have s, x, y as limit terms, although, of course, such a supposition would appear at first sight justified. That the numerical values of x, y in the p_{12} set are correct there can be no doubt, but it does not follow that they represent true terms. This may be illustrated by Ex. 8 of table ii., represented in map XL., which shows a set shifted from the $p_{1,2}$ set by the e link, even from the $P_3^4(1)$. The close lines shown there seem to represent displacements 2.49, 5.00, 4.81 being shifts on $p(1)$ terms due to two and four own displacements. The line [4] is a supposed normal line producing (3) by displacement, $3\delta_1$ on p_2 shifts 3.75. It is seen that the small shift required produces three correct links v, θ , and $2u' + u$ to (6). It is interesting to notice that (5, 6) are spark lines shifted e from a forbidden $D_{21}(j=1 \text{ to } 3)$, while that corresponding to P_1 is wanting. The significant point here is that we have a case where the $\theta\phi$ occur, and yet the limits must definitely be e less than s, x, y . The set is considered in more detail in § 10 in connexion with quartet B. Another illustration occurs in map XII., where the A, B (1, 2, 5, 6) sets are found with another corresponding one e ahead, consequently with limits e larger, although the ϕ separation is reproduced.

We can only settle the limits in each case by determining

one term from other considerations, such as, for instance, the linkage maps or summation lines. We shall, however, refer to the three columns of table i. respectively as the s , x , y columns.

We have this term indication for the sets $p_1, p_2 - p_h - Q$. $p_1 p_2$. They give the values $s = 63208 \cdot 12$, $x = 49062 \cdot 77$, $y = 51105 \cdot 64$. Any summation lines belonging to this set will lie in the unobserved region between the shortest of Bloch and the longest of Millikan and Bowen*.

p_h . This is generally regarded, after Randall, as the $p_1(2)$ corresponding to the preceding $p_1(1)$. Indeed the Z.P. for the y lines are the same, $0/1 \cdot 10$ for $y - p(1)$ and $0/1 \cdot 12$ for $y - p_h$. The limits are then the same x, y . Moreover, the $y - p_h, x - p_h$ behave similarly as to absorption by vapour (see (4), p. 1165), for whilst $x - p_h$ does not show the effect, $y - p_h$ is in Stücklen's class iii. With $x - p_1 2 = 36137$ there is no indication for $x - p_2^2$, which should be about 67 behind it. For a summation scheme we find :

(10 r) 38180·15	2042·58	(8) 36137·57	13245·50 (4x)	49383·07
51105·23		49057·3 - 19 dλ		
(1) 64030·32	2053·2 + 38 dλ	(2) 61977·1 - 33 dλ		beyond obs. region

Note.—Ultra-violet W.N. given to two decimal places are from observations by L. and E. Bloch; observations by Handke and others are given to one decimal place.

Here the y -summation is exact within O.E. The x -summation is also within the possible errors ($d\lambda = \cdot 25$) of McLennan's measure $\lambda = 1613 \cdot 5$, but this is possibly a merge (see quartet I. below).

The defect $\cdot 30$ in the $2042 \cdot 58$ is real, and can be explained by our shift on $p_1(2) = \cdot 326$.

Q. If the allocation† of $s - Q$ to P (3) is justified, the limits should be the actual x, y . In agreement with this we find the following summation set :

2, 43825·52	2043·24	8R, 41782·28	13246·2	1, 55028·5 - 30				
51102·3 + 17 dλ		49059·04		62298·8 + 20				
2, 58379·0 + 34 dλ	2043·2	00, 56335·81	13233·29	00, 69569·10 - 5				
{	0, 56291·41	44·40	00, ... 335·81	35·56	00, .. 371·37	39·11	0, ... 410·48	Bl.
	6, 56317·7	41·2	2, ... 358·9	44·5	3, ... 403·4	44·6	4, ... 448·0	Hke.
	00, 69569·10	33·40	00, ... 602·50	37·80	00, 640·30			Bl.

* Phys. Rev. 23, 1, 24.

† Phil. Mag. 39, 479, 20; 'Analysis, p. 254. This $p(3)$ is not in the same sequence as p_h .

Here the first two sets gives mean limit about 3 too small. The agreement of Handke's defective y -limit with that of Bloch's x is a curious coincidence, as the former's possible errors are considerable. The x, y limits definitely show a depression of 3.7. The s limit shows a further depression of 5.6 ($d\lambda = .2$ excessive for B/).

Round the x, s summation lines are seen successive close lines (given above) separated by roughly equal amounts. In general such successions indicate the presence of collaterals, in which case the summation lines may themselves be displaced, or the displacement may occur in the difference lines, the shift required in the x -line being 7.46. The latter supposition is supported by the succeeding F discussion.

If the displacement takes place in the Q term the own shift is the same for all three lines; if in the limits that for s would be 1.43 times larger than that for x , but the O.E. are too large to get any definite decision: $3\delta_1$ on x shift 7.20.

F. The F lines are 243.59, 243.80 behind Q, mean = 243.70. We find

8R 43581.72	2043.52	6, 41538.70
(50854.14)		48811.25
(58126.57)	(2042.76)	3, 56083.81

Here the x -limit is $x - 251.52$ with good measures. As the c -link is 251.39 [I. p. 200], it means that F is linked to a normal Q by $c = Q - c$. The limit is 247.79 less than that given by the Q summation set above, and this cannot be 248.44 within O.E. If Q be displaced 7.46, as indicated above, the normal $F - Q = 243.70 + 7.46 = 251.16$, in striking agreement. Thus $x_F = c \cdot x_Q + 7.46 = c\{x - p, 3\}$. There is no observed line for $y + F$, but there are two—sep. 127.37—equally and oppositely displaced from it, viz., 58062.91, 58190.28. Treating the displacement as $25\delta_1$ on a y term, direct calculation gives for the undisplaced line

$$58062.91 + 63.68 = 58126.59$$

$$58190.28 - 63.72 = \dots\dots 58126.56.$$

The mean is entered above, and the resulting limit is $y - 251.52$, corresponding to the observed $x - 251.52$.

9. In the three preceding cases we have quite definite indications from summation lines that in them we are dealing with pure difference lines in which 49062, 51105 behave as single terms. Moreover, the presence of displacements

exactly depending on 51105 as a single term $= R/(1.464963)^2$ practically proves that y at least is a real term. *But in none of the other lines in Shenstone's list* do we find any summation lines corresponding to s, x, y limits. That such lines have not been seen does not, of course, prove that the limits are not s, x, y , but taken in combination with the fact that, as we shall see, summation lines for other allocations do occur in considerable numbers, we are left to suspect that for these sets the true limits are different from s, x, y .

To allocate these lines recourse must be had to the maps of [I.]. We begin with the x -A, x -B lines, which are satelloids 5, 6 of map I. These are linked or collaterally related with the p_c and E sets. The inter-connexion—with some other linking—is shown in map XII., which explains itself. We note again here the repetitions of the e, u links found in the maps generally, especially in map VI. The separations 11 (at 3, 7) correspond to changes of a link from u to v or *vice versa*. The separation 149 is the old familiar 3*b* displacement on a p term. If we use the notation x A, y B, etc., to distinguish the sets, we note that in the x -chain—1, 2, 3, 4—we get first a $u'.v$ interchange 12.02 and then the 3*b* displacement, whereas in the y -chain—5, 6, 7, 8—we find the same in reversed order, with u, v interchange 11.45.

From 6 i [I. p. 223]

$$xB = e.P_1.v + 10x - y - .02,$$

the x, y^* having definitely entered through actual satelloids. We shall take $u' = u - y = 680.06$ to represent Rydberg's separation.

Then
$$xB = e.P_1.u'.v + 10x - y + .03.$$

The line indicated by (3) on the map is less by 11.97 = change of v to $u' + .05$. Hence

$$(3) = e.P_1.2u' + 10x - y + .08.$$

Note that the v already existed in the xB , to be changed to u . The first red satellite of xp_c is 147.53 ahead. It is therefore $e.P_1.2u' + 10x - y + 147.61$.

Now 3*b* on p_1 shifts 147.64 [I. p. 236]. Hence the satellite is $e.P_1(3b).2u' + 10x - y - .03$. It is a y -satelloid

* x, y are not arbitrary, but definite modifications, entering through satelloids, due to an unknown source in $s(1)$ or $p(1)$ terms; y can also enter through $u' = u - y$. Numerically $xA = e.P_1(\delta).v - .13$.

with the first red satellite at a distance $4y + \cdot 03$ [I. p. 198]. Hence

$$\begin{aligned} \mathbf{x}p_c &= e \cdot P_1(3b) \cdot 2u' + 10x + 3y + 0 \quad (\text{direct calc. gives } + \cdot 02) \\ &= e \cdot P_1(3b) \cdot 2u + 10x + y + \cdot 02. \end{aligned}$$

Now $\mathbf{x}p_c$ appears in 17 ii in a false cycle [I. p. 224]. The present argument shows that the separation 129.54 between satellites in the map is not an "L" separation as taken in [I.], but, with various satellite differences and u, v interchanges, corresponds to a $(3b)$ displacement. Map II., as developed from this, then proceeds with 18 ii, which is $u + \cdot 14$ ahead, and gives

$$18 \text{ ii} \equiv 31979.44 = e \cdot P_1(3b) \cdot 3u + 10x + y + \cdot 16. (d\lambda = \cdot 01).$$

Note that the $3u$ link here enters implicitly.

$sp_c(18)$ is $\theta + y + 0$ ahead of $\mathbf{x}p_c$. We find thence in 24 xii a line $e + 11.60$ ahead, the 11.60 changing $2u$ to $u.v^*$, and giving

$$(24) = P_1(3b) \cdot u.v \cdot \theta + 10x + 2y + \cdot 17 (d\lambda = \cdot 008).$$

The important result follows that with A, B, p_c the " \mathbf{x} " limit is not \mathbf{x} , but contains $s(1)$; the A, B terms are both $p_1(1)$, and p_c is $p_1(1)(3b)$. Coming now to the \mathbf{y} column, it is seen that the chain appears as in map III., Nos. 5, 7, 13 α , 13. This map is a composite of three distinct chains without definitely indicated relation to one another or to map I. We see now that this was due to the neglect of the 2042 separation. The guess which was attempted in the discussion of map III. is not therefore sustained. Also the limit in $\mathbf{y}A$ is not \mathbf{y} , but that of $\mathbf{x}A + \phi$, where now $\phi = 2042.87$ behaves as a link, or as the difference of two terms $\mathbf{y} - \mathbf{x}$. It means a complicated change taking place in the atom represented by the simultaneous fall of two electrons, one from $p(1)$ to $s(1)$, the other from \mathbf{y} to \mathbf{x} , and at the same time the configuration changes producing the u, e links. The formulæ are

$$\begin{aligned} \mathbf{y}A &= e \cdot P_1 \cdot v \cdot \phi + 10x - y - \cdot 02, \\ \mathbf{y}B &= e \cdot P_1 \cdot u.v \cdot \phi + 10x - 2y + \cdot 03. \end{aligned}$$

Any summation lines would lie in unobserved regions.

The map also shows that E belongs to the same system,

* For other examples of $u.v$ interchange, see sp_b below; also 8, 9 iii, amongst many others.

which explains why A, B, E show no θ -linked lines. x_E is $\phi + 11.41$ ahead of x_{p_c} , where $v - u = 11.45$. Hence

$$x_E = e.P_1(3b).u.v.\phi + 10x + y - .02.$$

y_E is $\phi - .17$ ahead, definitely not $y - x$; x_E is an x -satelloid [I. p. 198], and y_E a Stücklen satelloid :

$$\begin{aligned} y_E &= e.P_1(3b)u.v.2\phi + 10x + y - .19 \\ &= (...10y + .08 \text{ per sat.}). \end{aligned}$$

x_{p_d} is 371.607 ahead of x_{p_c} . This separation occurs very frequently not only in the B. Sh. quartet systems, but in many other instances. Intermediate lines in many of these cases (§ 15) show that it is a composite of 2X links forward and a displacement $-b$ on a p_1 term. The X links are generally distorted, but form a series inequality. Here the chain given in the diagram contains the two separations 221.49, 200.50 with the lines $1n, 31520.17$, $1n, 31720.66$. They would certainly not be recognized as X links*, but the character of the lines ($1n$) suggests displacement, and the 371 being a composite. The other cases suggest that they are the distorted representatives. But there is some evidence, given below in p. 1197, that 371 may be a true term difference. Whether that is the case or not, we shall take the 371.61 as formed in the same way as in other cases, as indeed the associated chain from sp_c to sp_d also shows. Now p_c depends on $P_1(3b)$ and $-b$ on $p_1(3b)$ shifts 49.10, so that $2Y_1$ and the $-b$ give $420.42 - 49.10 = 371.32$. Hence

$$\begin{aligned} x_{p_d} &= x_{p_c} + 371.61 \\ &= e.P_1(2b).2u.2Y_1 + 10x + y + .31(d\lambda = 0.3) \end{aligned}$$

(if exchanges of x, y were permissible, the residual might be $11y + .01$).

The observed 50.38 from x_{p_d} is an extra own displacement, making 50.33.

p_g . This is 3209.52, 3210.190, 3209.921 behind p_h , of which 3210.19 is the best measure. The θ value suggests the y for the variation in sp_g , and x_{p_g} is a satelloid. $3e + Y_1 = 3209.61$ and $+y = 3210.18$.

An intermediate $3e$ exists, viz.,

$$x_{p_g} \quad 3e + .04 \quad 3n, 35926.89 \quad Y_1 + y - .10 \quad 36137.57.$$

Also it is 425.58, .44 behind E. $2Y_2 = 425.05$ and

* [Added in proof. Distortion met by (25) being $x_{p_c} + Y_1 + \text{change of } 2u \text{ in } p_c \text{ to } u.v$].

$+y = \dots \cdot 65$. There is no intermediate; but they cannot both be right, for p_h depends on $p(2)$ and E on $p_1(1)(3b)$. We shall get quartet and summation evidence below (see notes to quartet J) for the first supposition, in which case

$$\mathbf{x}p_g = \mathbf{x} - 3e - Y_1 - y - \cdot 01 - p_1(2) \quad \text{or} \quad 45852\cdot 59 - p_1(2),$$

but the evidence here for this is not conclusive. It brings the p_g into the same category as p_1, p_2, p_h, Q, F .

p_a . $\mathbf{x}p_a$ is 38vi, but it enters by a link $u - 1\cdot 66 = a - 3y$, and cannot be regarded as certain. If the arrangement in the map be admitted—and the own multiple law considered below (quartet J) supports it—

$$\begin{aligned} \mathbf{x}p_a &= 2X_2 \cdot e \cdot Q^*(-a-b-\delta) \cdot u' - \cdot 06 \\ &= 2X_2 \cdot 4e \cdot P_1(-a-b-\delta) \cdot v + \cdot 19, \end{aligned}$$

$$a + b + \delta = 37\delta = (6^2 + 1)\delta,$$

and the Z.P. shows that p_a is probably a p^4 term.

p_b . p_b is 829·217, ·794 ahead. The difference of the two values is real, and is met precisely by y . We shall find other examples of this separation (§ 15), which is $u + 3b$ on a p term. Indeed, here we find an intermediate for xp , viz., 27015·48, with separations 682·85 and 146·92. Here p_a depends on $p_1(-37\delta)$ and $3b$ on this shifts 148·97, so that $u + 3b$ shift = 680·63 + 148·97 = 829·60. Hence

$$\mathbf{x}p_b = 2X_2 \cdot 4e \cdot P_1(-a + 2b - \delta)u \cdot v + \cdot 39 = \dots + y - \cdot 18,$$

$$\mathbf{s}p_b = 2X_2 \cdot 4e \cdot P_1(-a + 2b - \delta)u \cdot v \cdot \theta - \cdot 10.$$

There is, however, here also some evidence in favour of 829 being a true term difference (see quartet J below).

In passing we note here some further instances of exchange of u, v links:—

sp_b	40943·24	125 39	$1u$, 41069·13;	$\mathbf{x}p_b$ 27698·33;	$\mathbf{y}p_a$ 28911·40
	11·33		12 32	-11·55	-13·10
$1n$, 40954·57	126 88	$1n$, 41081·45;	2 , 27686·78;	1 , 28898·30	

These are $v - u - \cdot 12$, $+y + \cdot 30$, $+ \cdot 10$, $3y - \cdot 06$. The first two lines are the corresponding p_b with $2v$ for $u \cdot v$ and residuals $-\cdot 22$, $2y + \cdot 22$; the third changes $u \cdot v$ to $2u$; the last changes v to u with $-3y + \cdot 25$. We can get either interchange in p_b , since it involves $u \cdot v$, but in p_a the change v to u only can take place, and the observations meet these conditions. Moreover, the entrance of the y is explained by $\mathbf{y}p_a$ and $\mathbf{x}p_b$ being satelloids.

* Q of map VI. and p. 219 [I.].

The sets M, K, J, N, R. We note : (1) The lines suggested by Shenstone for the *s* column for M, K, J show O-C errors greater than the possible, except just possibly for J. We conclude that M, K, N, R do not show the θ separations. (2) The intensities and characters of $\mathbf{x}(K, N, R)$ and $\mathbf{y}M$ are the same, and all in Stücklen's class i. like the *s* lines, whilst the J are of intensity $1n$ and $\mathbf{x}J$ is in class v. (3) K has no \mathbf{y} representative, and those suggested for N, R are very doubtful, with intensities abnormally small. (4) In the case of M it is the \mathbf{y} -line which is analogous in character to \mathbf{x} of K, N, R.

We must draw the conclusion that the K, N, R are of closely allied nature, and possibly M (or $\mathbf{y}M$ placed in the \mathbf{x} -column) may belong to the same category, whilst J is entirely unrelated to them.

$\mathbf{x}J$ (20 xii) is $sp_d - 211.98 = e.P_1(2b).2u.X_1.\theta + 7x + 3y + .01$.

K. $\mathbf{x}K$ is $1999.87 = 2e + .27$ behind $sp_g = 5e + Y_1 + .18$ behind sp_h .

$$\therefore \mathbf{x}K = 5e.Y_1.P_1(2) - .18.$$

Any summation line would lie about 70024, amongst the extreme lines of Bloch.

N. H. and K.R. make this 700.87 ahead of $\mathbf{x}K$, and the recent more accurate values of Wolfsohn make it 700.19. This is $Y_1.2Y_2 + (\Delta)$ on $P_1(2)$, where the Δ shifts 64.60. Taking W.'s wave-number in air, 44873.825 gives

$$\mathbf{x}N = 5e.P_1(2)(\Delta).2Y_2 + .07.$$

R. Here W. agrees with H. (.32 for .39), and makes it 245.50 ahead. Now the "a" link is 245.54 [I. p. 200]. Hence

$$\mathbf{x}R = 5e.P_1(2)(\Delta).2Y_2.a + .03.$$

M. $\mathbf{x}M$ is 1075.34 behind K. (2b) on $P_1(2)$ shifts 25.88, and $-u - 2Y_1 + 2b$ on $P(2) = -1101.05 + 25.88 = 1075.17$.

$$\begin{aligned}\therefore \mathbf{x}M &= 5e.Y_1.P_1(2)(2b) - u - 2Y_1 - .07 \\ &= 5e.u.3Y_1.P_1(2)(2b) - .07\end{aligned}$$

$$\text{or} \quad = 5e.u.3X_1P_1(2)(2b - \delta) + .23.$$

$\mathbf{y}M$ is $2042.67 = 3u + .78$ ahead,

$$= 5e.3X_1P_1(2)(2b).2u - .28 \text{ (W.) or } +.30 \text{ (H.)}.$$

Either of the alternative forms for $\mathbf{x}M$ will meet the case, but the second explains why $\mathbf{x}M$ is of abnormal character,

and the vapour-absorption of \mathbf{yM} is seen as a consequence of its dependence, like \mathbf{K} , \mathbf{N} , \mathbf{R} , on pure multiple b displacements. All these lines $\mathbf{M} \dots \mathbf{R}$ must therefore be transferred to the s -column.

p_e, p_f . Difficulties occur in the allocation. The θ separations are too large, and the intensities of the (s) lines ($1n$) compared with the (\mathbf{x}, \mathbf{y}) show a distinct anomaly when compared with those of the other sets. We cannot be certain, therefore, that the (s) and the (\mathbf{x}, \mathbf{y}) belong to the same system. sp_e is 680.83 ahead of \mathbf{yM} , so that

$$sp_e = 5e \cdot 3X_1 \cdot P_1(2)(2b) \cdot 3u - \cdot 08,$$

with the same authority as \mathbf{yM} . sp_f is 58.24 ahead, which we naturally regard as due to a new term, *i. e.*, to displacement on $p_1(2)(2b)$. Now 458 on this shifts 58.00, so that

$$sp_f = 5e \cdot 3X_1 \cdot P_1(2)(65\delta) \cdot 3u + \cdot 16.$$

It is not dependent on the a, b multiples which we have found so prevalent. On the other hand, as $65 = 8^2 + 1$, it is an example of a δ multiple condition already frequently met with. With these allocations the (\mathbf{x}, \mathbf{y}) lines fall in by interchange of \mathbf{x}, \mathbf{y} for s , and we get a very satisfactory system. But certain difficulties appear. xp_e is 16 iii; it is 49.02 from the outer satellite of 5 iii—*i. e.*, of \mathbf{yA} , which depends on $P_1(1)$ and b on $p_1(1)$ shifts 49.31. Now although exact links frequently depend on satellites, pure displacement shifts are rather exceptional, so that this allocation is in itself doubtful, apart from the magnitude of the residual. If not accepted, the link 50.75 in map III. must be marked false. If accepted, it gives $xp_e = e \cdot P_1(b)v \cdot \phi + 15x - y - \cdot 18$. Also xp_f is connected to \mathbf{xB} by a chain from xii to xiii, viz.,

$$\mathbf{xB}, 11, 35 \text{ xii} = 14 \text{ iii}, xp_f,$$

$xp_f, 11, \mathbf{xB}$ all being sateloids. The result is

$$xp_f = X_1 \cdot P_1(1) \cdot 2u \cdot v + 12y + 02.$$

This has clearly no connexion with the former xp_e . If it be accepted, the -58.44 to xp_e would be met by a change of v to u and a displacement $-b + 2\delta_1$

$$\text{and } xp_e = X_1 \cdot P_1(1)(-b + 2\delta_1) \cdot 3u + 12y + \cdot 03.$$

The symmetry of the map speaks strongly for the reality of the whole chain. If it is not real, the false link must be the 208.27 between 11, 35 xii, but the successive \mathbf{X} links are of great frequency in this map, and we get here a series

inequality $208.27 + 211.50 = 2X_1 + 0$. The question must be left open at present.

The results are here collected (satellite y etc. omitted).

- i. The s column contains s (1) in the limit value, and the others are found by putting x, y for s . The s value only is given.

$$p_1, p_2 = P_1(1), P_2(1)$$

$$p_h = P_1(2)$$

$$p_g = 3e \cdot Y_1 \cdot P_1(2)$$

$$p_e = 5e \cdot 3X_1 \cdot P_1(2)(2b) \cdot 3u$$

$$p'_f = 5e \cdot 3X_1 \cdot P_1(2)(65\delta) \cdot 3u$$

$$Q = (3\delta_1) P_1'(3)$$

$$F = c \cdot P_1'(3)$$

Here P' refers to that P series, which produces also the lines $p1 - pm$ (Analysis, pp. 254, 256).

- ii. The lines are to be transferred to the s column.

$$A = e \cdot P_1(1) \cdot v$$

$$yM = 5e \cdot 3X_1 \cdot P_1(2)(2b) \cdot 2u$$

$$B = e \cdot P_1(1) \cdot u \cdot v$$

$$K = 5e \cdot Y_1 \cdot P_1(2)$$

$$E = e \cdot P_1(1)(3b) \cdot u \cdot v \cdot \phi$$

$$N = 5e \cdot P_1(2)(\Delta) \cdot 2Y_2$$

$$J = e \cdot P_1(1)(2b) \cdot 2u \cdot X_1 \cdot \theta$$

$$R = 5e \cdot P_1(2)(\Delta) \cdot 2Y_2 \cdot a$$

- iii. Lines apparently forming s lines by addition of θ link to x lines. The x lines are given.

$$p_a = 2X_2 \cdot 4e \cdot P_1(1)(-a-b-\delta) \cdot v$$

$$p_c = e \cdot P_1(1)(3b) \cdot 2u$$

$$p_b = 2X_2 \cdot 4e \cdot P_1(1)(-a+2b-\delta) \cdot u \cdot v$$

$$p_d = e \cdot P_1(1)(2b) \cdot 2u \cdot Y_1$$

The abnormality in this last class means that the s lines contain $2s$ (1) or that θ is a pure link. This is not easy to believe; but that θ, ϕ do appear in a way similar to that of links is shown by the existence of successive θ and ϕ values, although the evidence for θ is not very satisfactory, since the lines involved lie in the far ultra-violet with poor measures. Some cases are seen in map XIII., viz., $x p_e$, $s p_e$ (3), and $x p_c$, $s p_c$ (15). There are several successive ϕ and θ from ϕ separated lines difficult to explain if ϕ is a pure term separation. For one very definite instance of $\theta\phi$ see note to 26, 30, 42 of line-list for map XII.

A possible source of θ should perhaps here be put on record. Of the P' series referred to above, $P_1'(2)$ is 2037.22 (K.R.), 30 (McL.), $n=49068.73$ (McL.), close to x . We saw above that Q indicated a value about 7 smaller, and there is independent evidence which cannot be taken now. It gives

$$p_1'(2) = 13239.40 + 24 d\lambda \text{ or } + 7 = 13246. = \theta \text{ within O.E.}$$

So $x p_1 = s - p_1'(1) - p_1'(2)$, indicating a fall of one electron from $p(1)$ or $p(2)$ to s , accompanied by a simultaneous expulsion of one from $p(2)$ or $p(1)$ to a peripheral level. On the contrary, in class iii. the s column is formed by adding $p(2)$ to the x column, and the second electron falls from the periphery to $p(2)$ or $p(1)$. In passing, it is interesting to note that opposite own displacements on $p(1)$, $p(2)$ produce shifts about $\pm .59$ or y .

With this would go the assumption that y is a true term limit, and we should understand why the $x p$ lines are enhanced by the spark and the $y p$ weakened.

Quartets.

10. It is noticeable that, amongst the ultra-violet spark lines of Handke and of W. and E. Bloch, a very considerable number show not only the neutral atom links, but also separations 2042, 1412, and even 13245, or values close to them. They are therefore radiated by the neutral atom, and can have no relation to the ionized atom. We shall later have occasion to notice some of these 2042, 1412 separations, but it may be useful * here to give some examples of the presence of neutral links. The examples are taken from measures of L. and E. Bloch only, whose O.E. amount to only a few units of the second decimals in ångströms. The $d\lambda$ on the links are given in ().

TABLE III.

3, 56083.81	e+1.83	4, 57085.44 (.05)	5, 58722.66	e-.65	6, 59721.81 (.02)
1, 56975.18	e-.26	1, 57974.72 (.008)	5, 58752.34	u+.98	3, 59433.95 (.03)
3, 58436.47	v-.15	0, 58684.76 (.00)	1, 59219.51	e-.11	1, 60219.20 (.00)
6, 58518.20	v+.20	3, 59210.48 (.00)	0, 59455.15	2042.82	4, 61497.97 (.00)
				13236.69	1, 72691.84 (-.17)
1, 60986.77	-u'+0	4, 60306.71	e-.07	1, 61306.44 (.00, .00)	
3, 62275.80	u+1.20	1, 62957.63	v-.04	1, 63649.67 (.03, .00)	
3, 62219.24	e+.47	00, 63219.51	2048.68	$2\nu\nu$, 65268.19 (.01, .14)	
4, 62247.12	e-.61	$2\nu\nu$, 63246.31	2042.76	00, 65289.07 (.01, .00)	
4, 64790.76	-2040.55	5, 62750.21	e-.51	1, 63749.50 (.05, .01)	
1, 64043.04	v-.98	1, 64734.14	$X_2+.04$	0, 64946.45 (.02, .00)	
12, 64146.25	v-1.05	2ν , 69837.28	-2040.67	1, 67796.61 (.02, .04)	

The number of examples giving values exact within O.E. excludes an explanation of chance coincidences. Several of these ultra-violet lines almost at sight fall into quartet

* In view of the current obsession that "spark spectra" and "spectra of ionized atoms" are convertible phrases.

arrangements. From their high wave-number they must correspond to summation sets, and in some cases the corresponding difference quartets can be indicated. The ease with which they are recognized depends on the fact that neutral lines amongst them can consist of summation lines alone, and are only confused by the presence of radiations due to ionized atoms. But it is curious that some of these lines—especially in Handke's longer wave-lengths—are much more intense than others and than the corresponding difference sets. This is perhaps explained by the fact that these latter show irregular separations, small intensities, and parallel repetitions which suggest that they are not of a fundamental type, but are displacements from such. *E.g.*, in the quartets C, D below we clearly get two of similar nature mutually shifted by an amount of about 24·6.

We consider first the lines involved in map XI., linked to our first quartet A (§ 4). That it contains a few spark lines is explained by the linking. We have seen that the P, D' lines have a parallel set at a distance $-e$ (4, 6, 7, 8, 2), even the "forbidden" line D_{21} being so reproduced. But the quartet depending on these is not found. Traces, however, of such a quartet appear shifted a distance $-e + 1412·7 - 243$, the 243 being the doublet separation $248·44$ with a displacement $-\delta$ in $p_1(1)$ shifting 4·94 (obs.=4·81). They are arranged here in quartet form, the lines being represented by the numbering in the map.

	(10)	1411·09	(9)	896·98	(16)	
	248 30		248 83			B.
(14)	2042·25	(13, 11, 12)	1413·05	(3)		

(16) is too strong; it does not reproduce the 894, and should probably be omitted. It is noticeable that, while the P are parallelized by $-e$ excluding P_{11} , and the doublet D set by $-e$ including the forbidden D_{21} , the quartet D are parallelized by $-e - \nu + 1412 = 164$.

The next instance we take is one which is specially interesting because it gives indications of a series which closely follows an exact Rydberg sequence. Consider the $m=3$ set in the following list of difference-summation lines.

<i>m.</i>	<i>y.</i>	<i>x.</i>	<i>s.</i>
	4n, 30825·261	3, 28792·500	—
	2032·75		
2 {	51093·27	49063·10	
	00, 71361·29	00, 69333·70	outside obs.
	2027·59		

<i>m.</i>	<i>y.</i>	<i>x.</i>	<i>s.</i>
	1 <i>n</i> , 41201·65	1 <i>r</i> , 39153·26	0 <i>d</i> , 52398·82
		2048·39	13245·56
3.	51107·2	49062·2	62305·65 - 26 <i>dλ</i>
	1, 61012·8 (McL.)	1, 58971·2 (Hke.)	00·72212·49 - 52 <i>dλ</i>
		2041·6	13241·3
	45242·09 (P.R.)	[43204]	4, 56448·0 (Hke.)
		2038	13244
4.	51106·49	(49058·8 - 15 <i>dλ</i>)	
	1, 56975·18	1, 54913·7 - 30 <i>dλ</i> (Hke.)	—
		2061·5 + 30 <i>dλ</i>	
	0, 47236·60 (P.R.)	[45197·34]	—
		2039·3	
5.	51105·3		
	1, 54974·0 (Hke.)	—	—

Possibly for $s \mp t(6)$; calc. [59568] 62308·5 1, 65049·1 (McL.)

Here K.R. = Kayser and Runge. Hke. = Handke. McL. = McLennan.
P.R. = Pina de Rubies.

$m=2$. The 71361 of Bloch agrees with the calculated with $d\lambda = -.06$.

$m=3$. 41201 comes in a long sequence of 1*n* lines suggesting displacement.

$m=4$. The 54913 by Hke. requires a possible correction $d\lambda = -.2$. 56975 occurs also in quartet D below.

$m=5$. The *y* lines give exact mean limit, but require corrections $d\lambda = -.16$. 09 to agree with the Rydberg formula. Pina de Rubies gives a series of successive lines at regular intervals before and after $y-t(5)$, viz. :—omitting the 47,

0, 133·93	0, 159·28	0, 185·77	3, 211·17	0, 47236·60	2 <i>n</i> , 263·62	4, 286·65	4, 308·57
25·35	26·490	25·40	25·43	27·02	23·03	21·92	

If the *y* be a true term, 10 δ , displacement shifts 25·49, whilst δ on $t(5)$ shifts 21·2. The shift 27·02 is $(-10 \delta_1)/(7 \delta) + .05$, but as the line involved is of a different character (2*n*) from that of the others, it possibly does not belong to the system. If we denote 47236 by Z the series of lines are :

$$(40 \delta_1)Z(-4 \delta), (30 \delta_1)Z(-4 \delta), (20 \delta_1)Z, (10 \delta_1)Z, Z, [(-10 \delta_1)Z(7 \delta)], \\ (-20 \delta_1)Z(-4 \delta), (-36 \delta_1)Z.$$

Direct calculation shows the first to be 102·66 behind Z as against observed 102·67 and $(-36 \delta_1)Z$ as 91·86 ahead as against observed 91·97 ($d\lambda = .005$).

Here we find the *s*, *x*, *y*, limits exact within O.E., and the exact θ separation. The O.E. in 39153 is small, and the mean limit is very close to exact *x*. Taking it as $x-t$, *t* is found to be

$$t = 9909·51 = R/\{3·326863\}^2.$$

Now the denominator for S(1) is 1·326748, the same mantissa within O.E. If *t* be corrected to the same mantissa, the wave number should be .68 less or K.R.'s measure .04 A

larger. It suggests the existence of series with current term following the Rydberg formula,

$$t(m) = R/\{m + \cdot 326748\}^2.$$

The calculated values for the x series are entered in the list in [] for $m=4, 5$. No observed lines are found for these, but they exist for y , in $m=4, 5$, for s in $m=4$, and possibly $m=6$.

The calculated values for $x \mp t(2)$ are 28803·53, 69322·01. They are not found, but $y + t(2)$ is given by Bloch with error $d\lambda = -\cdot 06$. The lines in the list, however, are close to these and give the true x limit within O.E. The $x - t(2) = 28792\cdot 50$ has a very small O.E. and gives mantissa $a = 326114$ or 634 too small. Thus either the Rydberg is not exact or displacements occur in $m=2$, indicated, indeed, by the defective ϕ separations. We leave the matter here as it has little bearing on our present discussion apart from the summation evidence. Details are given in the notes appended to the list. We should expect the forbidden column $s(1) - t(m)$ to show lacunæ. But the most interesting point is that the x, y set in $m=3$ form the starting-point of a quartet, accompanied by a collateral one. They are :

C.

j .	4.	3.	2.	1.
1			2, 38312·88 _s	1 _n , 37413·35 (E.H.)
			899·53	
			263·33	242·18
2	1 _n , 39468·57 _s	1, 38049·55	4 _n , 37171·17 (Hp.)	
		1419·02	878·38	
		315·31	322·63	
3	1 _n , 41201·65 *	1 _r , 39153·26 *	1, 37726·92	
	2048·39	1426·95		
	51107·2	60·73 490 62·23	55·55 476 44·57 39·71 46765·03
3	1, 61012·8 *	1, 58971·2 *	7, 57552·5 (Hke.)	
	2041·6	1418·7		
		318·3	312·9	
2	2, 58652·9	6, 57239·6	2, 56358·9	
		1413·3	880·7	
			241·4	
1			6, 56998·2	[56098·8]

D.				
j	4.	3.	2.	1.
			2, 38312·87 s?	1, 37425·25 *
			887·62	
			252·2	230·56
	1n, 39480·89 s	1n, 38060·7 (E.H.)	1n, 37194·69 K.R.*	
	1420·2	866·0		
	307·7			
1n, 41226·28 *	1n, 39173·2 s (E.V.)	—		
51106·52	490 59·25 64·78	476 44·02 35·61	4675 4·53 6·20	
1, 60986·77 *	0, 58956·36	3, 57535·74		
2030·41	1420·62			
	318·75	325·21		
	6, 58637·61	3, 57210·53	6, 56317·7 * (Hke.)	
	1427·08	892·8		
		235·35	233·9	
		1, 56975·18	3, 56083·81 *	
		891·37		

The limit means are entered in the order corresponding to the difference lines above.

The normal values of the limits are

51105·64 49062·77 47650·0 46756·1

These were first recognized in the summation sets, and the difference indicated by them. We notice that the two difference quartets (say, Q_1 , Q_2) are composed of weak lines with some spark representatives, the second more affected by the spark than the first, also that the Q are more intense, and that while Handke observes the Q_1 , the stronger excitation of Bloch produces the Q_2 . The presence of spark lines in the Q also suggests displaced lines, and this is further sustained by those lines in the neighbourhood of the same character already given (p. 1176).

Those sets giving mean limits close to the normal y , x are indicated by an asterisk. Our discussion would be much simplified if we could be sure that the corresponding difference-summation pairs were real, *i.e.*, that any displacement present were common to both lines. Unfortunately, here with good measures in Q_1 we have Handke's considerable O.E. in Q_1 , whilst the good measures of Bloch in Q_2 are combined with irregular and defective observations in Q_2 ; also the own shift in the $t(3)$ term (·217) is so small that definite conclusions cannot be drawn. Nevertheless it will be instructive to test the observations on this supposition. Where the mean limit is normal within O.E. we may be justified in taking these limits as not displaced. In the first (C), for instance, the mean 49062·2 is correct within Hke.'s O.E. In other words, the lines 39153, 58971 may be taken

as correctly allocated as Z_{12} , \mathbf{Z}_{12} (say) and may be taken as our starting-point. As the small oun shift ($\cdot 217$) in $t(3)$ renders the small details of any scheme not fully convincing, it will be sufficient here merely to give the result. It is shown in the annexed table, the first scheme indicating the displacements which the observed lines in the first quartet have experienced, and the second giving the wave numbers of the normal Z quartet of which the observed are collaterals.

The numbers in brackets before the W.N. denote the $d\lambda$ corrections to be applied to the observed to make exact agreement (0 means $< \cdot 01$). It will be seen that this is complete within O.E., but in the \mathbf{Q} other values involving oun shifts in $t(3)$ might be taken, and the results be still within Handke's O.E., but no such latitude is allowable in the far more accurate \mathbf{Q} lines. The significant point is that all the corresponding pairs are each true difference-summation lines (*i. e.*, displacement the same). In the calculations the d separations have been regarded as composite and depending on the limit term \mathbf{y} (oun shift 2.549). If all the limits be regarded as single terms, the shift per oun would be 2.549, 2.398, 2.295, 2.230. The agreement is definitely upset, again in accordance with several previous indications that \mathbf{y} is a real term, and 2042, etc., are composite; in other words, all the real limit terms differ only slightly from \mathbf{y} . The discussion of this set has one very important result in fixing more closely the normal values of the 1412, 894, which as given in the first quartet (A) are uncertain within a few decimals owing to their dependence on Aretz's measures. The modifications by the oun shifts can be exactly determined, and it is then seen that we get perfect agreement for 1412.70 and 894.00 within very small O.E. in *all* the lines.

Displacements in C.

$$\begin{array}{ccccc} & & (-2\delta_1)\mathbf{Z}_{33}(2\delta_1) & & \mathbf{Z}_{34} \\ (-2\delta_1)\mathbf{Z}_{11}(2\delta_1) & (\delta_1)\mathbf{Z}_{22} & (2\delta_1)\mathbf{Z}_{23}(-4\Delta-2\delta_1) & & (-\delta)\mathbf{Z}_{34}(-4\delta) \\ & \mathbf{Z}_{12} & (\delta)\mathbf{Z}_{13}(4\delta) & & \end{array}$$

with the same scheme for \mathbf{Z} , but no \mathbf{Z}_{34} .

Resulting normal quartet:—

	2042.87	1412.7	894
248.9	(0) 39471.12	(0) 38307.35	(0) 37413.35
317.86	(0) 41196.13	(0) 39153.26	(0) 37740.56
\mathbf{Z}	(-2) 61015.15	(-0.03) 58972.28	(0) 57559.58
317.86	(0.03) 58654.42	(-0.01) 57241.75	(-0.08) 56347.75
248.9		(0.02) 56992.82	[56098.82]
$317.86 : 248.9 = 5 \times 63.5 : 4 : 62.2 = 5 : 4$			

In the second quartet the characters of the lines suggest that it and the first are collaterals, that is are displaced from a common normal one. The first, second, and fourth mean limits are so close to normal values that any displacement must lie in the current term. The equal and opposite shifts in Z_{11} , Z_{34} from those of the normal quartet— $30\cdot15$, $-28\cdot38$; $30\cdot3$, $-30\cdot0$ —proves this for these lines. It means a displacement of -35δ , shifting $30\cdot54$, within one or two oons ($34\frac{1}{2}\delta$ shifts $30\cdot11$). But nothing is to be gained at present by following this out in more detail.

The $m = 2$ lines of the same $s(m)$ Rydberg series also show relation to quartet forms. We find :—

E.

			$2n$, 27584·18	892·39	$2n$, 26691·79 (C. T.)
			132·22		133·4
	$1n$, 28864·28	1412·32	2 , 27451·96	893·06	1 , 26553·90 (C. T.)
	167·85		167·80		
2 , 30739·38	2042·95	4 , 28696·43	1412·27	$1n$, 27284·16 (C. T.)	
		$7\cdot77$			
$51111\cdot29$		4906			
		—			
00 , 71483·20					
		00 , 69271·27			

$$167\cdot83 : 132\cdot3 = 5 \times 33\cdot56 : 4 \times 33\cdot1 = 5 : 4$$

This pd quartet has a defective summation, but those present both give y , x mean limits 5 too great (2δ , shift on $y = 5\cdot10$). We note also that both the $m = 2$, $m = 3$ quartets give the same separation ratio 5 : 4.

We find a considerable number of sets throughout the whole spectrum separated by about 96. We find one here, for instance, with the observed $s(2)$, viz. (excluding the first line) :—

F.

	4 , 30939·65	2041·35	1 , 28898·30	1402·78	3 , 27495·52	903·73	2 , 26591·79
	85·60		105·80		112·51		109·4
$m=2$	$2n$, 30825·25	2032·75	3 , 28792·50	1409·49	1 , 27383·01	900·67	$3n$, 26482·36, s. (E. V.)
	$51093\cdot29$		$49063\cdot10$		$47651\cdot95$		$46755\cdot15$
	00 , 71361·29	2027·59	00 , 69333·70	1412·76	1 , 67920·94	892·99	3 , 67027·95
	00 , 71264·66	96·63					

The difference lines are respectively $85\cdot8$, $95\cdot87$, $96\cdot07$. $98\cdot85$ ahead of the Z_{11} of the E quartet. The Z_{11} , Z_{11} give too small a limit by $12\cdot35$, the others normal within O.E.

The 96 separations would be therefore current term displacements. The "forbidden" line 26482 is a spark line also, as it should be.

The first horizontal line in the above gives another parallel set, interesting because $2041.35 = 3u' - .17$ is a linkage value, and $1402.78 + 903.73 = 1412.7 + 893.8$, the true normal d -values. To further illustrate the 96 case, we may adduce the following fragmentary set:—

G.

		1, 34878.19 (E. H.)	
		98.21	
1n, 37012.22	2035.82	1, 34976.40	1409.90 2n, 33566.51
		2.25	
51102.54		4906	
		3.03	
0, 65192.87	2043.22	0, 63149.65	
96.20			96.66
00, 65289.07	2042.76	4nr, 63246.31	

H.

			4n, 21282.02	887.75	4, 22169.77
			312.51		
—		2, 19556.59	1412.92	2n, 20969.51	
		451.04			
1, 17068.77	2036.78	2, s, 19105.55			
552.08		(37, — vii)		(9, 15 viii)	(8 viii)
1, 16516.77					

$$552 : 451 : 312 = 9 \times 61.3 : 7 \times 64.4 : 5 \times 62.5 = 9 : 7 : 5$$

. Any summation lines with limits y, x are outside observed regions. The frame is of F^4 type. 22169 appears as F_{44}^4 . It appears also of the same type in a different quartet arrangement given by Beals, and by Shenstone. When later we discuss the latter we shall find that the Z.P. definitely sustains the allocation of this line. Further (though not in B. or Sh.), the f separations are in the correct ratios according to Landé's rule. The d separations are additive, *i.e.* the lines are of the form $f-d$, not $d-f$. Two constituents are missing. In other respects it is a good typical F quartet, except that the characters are not all alike or the intensities normally related. Also the F_{33}^4 , or 20969, has a Z.P. = 0/·69 (Sh.) which agrees with that for F_{33}^4 , viz. ·26, ·09/·77, ·94, 1·11. Sommer allocates this line to $d_1^2 d_1^2$, Z.P. = ·60, ·20/1·00, 1·40, 1·80, which it certainly is not :

Shenstone to 232-??3, which includes Sommer's. On the contrary, the Z.P. for 19556 or F_{23}^4 is given by both S. and Sh. as 0/0, *i. e.* is not affected by the magnetic field. This contradicts F_{23}^4 and is consonant with their allocation as $d_4^4 d_4^4 (j=1, 1)$ or indeed with any line not affected by the magnetic field.

11. We come now to the consideration of the quartet relations of Shenstone's lines, and begin with those which the previous discussion has shown to depend on the y , x limits, viz. :— $p_1, p_2; p_h; Q; F$ and probably p_g .

p_1, p_2 . These give the original quartet A which has served for the discovery of the 2042, 1412, 894 separations.

p_h . As p_h is $p_1(2)$ we should not expect to find such a complete set as for $p(1)$. Also no corresponding $p_2^2(2)$ occurs. The following arrangement, not altogether satisfying, would seem to indicate that p_h is a fourfold term also :—

I.

			1, 34777·40 (E. H.)	894	[... 83·40]
			1330		(1m, 33873·5)
	1 R, 36172·63	1408·55	1, 34764·10 (E. H.)		[... 66·0]
	35·08				
10, 38180·15	2042·87	8, 36137·57	—		
51105·23		[49062·51]	47653·7—18 $d\lambda$		(·46759)
1, 64030·32	2042·87	[61987·45]	1412·7	+896·0	1, 59678—35 $d\lambda$
	2, 61977·1—38 $d\lambda$				
	[... 56·0]	1412·7	6, 60543·31	889·7	2, 59653—35 $d\lambda$
			(7, 60537·0—36 $d\lambda$)		

In this [61987, ... 56] are calculated respectively from 64030 and 60543. McLennan's 61977 is the mean, and would represent their merge, $d\lambda = 1·4$. [33883, ... 66] are calculated respectively from 34777 and 36172. Again, their merge might be represented by 33873. 59653 gives the correct separation within O.E. It is "forbidden," but a spark line. Handke's 60537 may also be a merge of 60543 and Z_{33} , or it may just possibly be his measure for Bloch's line ($d\lambda = ·17$).

Q.F. These belong to $p(3)$. There are no traces of either a difference or summation quartet, except a just possible 1, 54913·7 by Handke, giving a separation 1422 with $x+Q$, and requiring $d\lambda = -·3$.

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J.

				1, 31455·18	
				24·57	
		1, 32890·81	1411·06	3n, 31479·75	891·39 3, 30588·3
		36·57; 39·55		40·42	
p_g 2, 34970·233	2042·85	6, 32927·382 (30·36)	1407·21; or	10·09	31520·17
630·28	1412·57	120·96; 117·98		115·80	
1, 34339·95		3, 33048·34	1412·37	2, 31635·972	896·59 2, 30739·38
				84·79	85·8
				1n, 31720·66	895·41 nn, 30825·2

(1) Appears also in quartet E.

We have here a double quartet, in one with direct terms 40, 24, the other with inverted 120, 84. The 32927 is a y satelloid, its extreme violet satellite in (). Indeed, the d separations seem affected with the y shifts. Thus

$$\begin{aligned}
 1411\cdot06 + 3y &= 1412\cdot77 & 891\cdot39 + 5y &= 894\cdot24 \\
 1407\cdot21 + 10y &= 1412\cdot91 & 896\cdot59 - 4y &= 894\cdot31 \\
 1412\cdot37 + y &= 1412\cdot94 & 895\cdot41 - 2y &= 894\cdot27
 \end{aligned}$$

In both quartets the portions after this line seem to depend on the satellite, and better even on one $2y$ further out. With this

$$39\cdot5 : 24\cdot5 = 5 : 3 \text{ and } 120\cdot96 : 84\cdot7 = 7 \times 17\cdot2 : 5 \times 16\cdot9 = 7 : 5.$$

The line 34339 is introduced as it gives 1412·57 *back* from 32927. This must be a coincidence and due to the fact that $1412 = 2042 - 630$, and the line is linked $-3Y_1 + \cdot35$ or $-X_1 - 2Y_1 + \cdot02$ with 34970.

If p_g is taken as $p_h - (3e + Y_1)$, as in § 23, the limit for x_{p_g} is $45852\cdot59$, and the summation for x_{p_g} would be $91705\cdot19 - 32927\cdot38 = 58777\cdot81$. There is no line here, but both Hke. and Bl. give a series of successive lines with nearly equal separations suggesting the presence of collaterals. Thus

	Bl.		Hke.
	39·68		37·6
58637·61	58752·34	58652·9	58763·2
47·15	39·71	44·80	48·4
684·76	792·05	697·7	811·6
37·90		37·9	
722·66		735·6	

The composite limit depends on y , in which $-10\delta_1$ shifts $25\cdot47$. Thus $(10\delta_1)58777\cdot81 = 58752\cdot34$, which is one of Bloch's lines. In the neighbourhood, however, is a very

suggestive copy of the difference quartet by Hke., exact within his O.E. Thus

		6, 56317·9	—
		85·5	
1, 57815·4	1412·0	3, 56403·4	—
	127·3	124·4	
—	3, 57942·7	1414·9	8, 56527·8

Fortunately, one of these is given by Bl., so that the absolute value of one can be fixed. Hke.'s 56527·8 is Bl.'s 4.56524·32. This gives the separation 120·9 with Hke.'s 56403. If we correct from Bl. by the correct separations as shown by the difference quartet, we get the following set, in which the figures in () give $d\lambda = \text{Bl.} - \text{Hke.} :-$

		6, 56318·7 (-·04)	[55924·7]
		84·7	
1, 57816·06 (-·02)	1412·7	3, 56403·3 (-·00)	[55509·4]
	120·96	120·96	
[59979·89]	3, 57937·02 (-·17)	1412·7	8, 56524·32 (-·1)

Here 57937 is 840·81 below the supposed correct summation 58777. This is $4Y_1 - \cdot 03$. Thus, while p is shifted $3e + Y_1$ back from p_h , this set is shifted a further $4Y_1$ or $3e + 5Y_1$ from $x + p_h$. It is probable that other linked sets may be present, for there are a considerable number of $e, 2e, 3e$ links in this region. The importance of this pair of quartets lies in the support it gives to the dependence of the p_g lines on p_h , *i.e.* on $p_1(2)$. If we could feel certainty as to the exactness of the two sets of separations 59·55, 24·57 and 120·96, 84·70, the own law would give practical proof of this dependence on p_h , for the respective mantissæ differences and own relations are as follows :—

$4441 = 30\frac{1}{2}\delta - 16\cdot3$; $2755 = 19\delta + 15\cdot8$ sum $= 49\frac{1}{2}\delta - \cdot 5$
 $13727 = 94\delta - 10$; $9728 = 66\frac{1}{2}\delta + 10$ sum $= 160\frac{1}{2}\delta + 0$,
 showing both the systematic triplet effect and the exact sum.

The foregoing have all been shown to depend on x, y in their limits. Evidence has also been given to show that the remainder of Shenstone's p -lines depend on $P(1)$, *i.e.* involve s in their limit values. We have been led to regard the separations between the pairs arranged by Shenstone as probably complex and due to combined links and a displacement on a p term.

p_a, p_b . We find

K.

2, 26771·70 890·72 1, 25880·98 (E. H.)

487·49

2, 27698·33 1414·12 1 n , 26284·21

829·795

3, 28911·40 2042·86

2, 26868·54

with sp_a 829·217

sp_b 492·94 1 n , 41436·28

$$829·2 : 492·9 = 5 \times 165·8 : 3 \times 164·3 = 5^{\circ} : 3$$

With the allocations adopted for p_a, p_b any summation lines would lie beyond observed regions. If the limits are y, x the only near one is 71264·66, which gives with p_a a mean 49066·6 definitely not x itself. But there are no other near lines falling in with the rest of the scheme, and it belongs to another set. It is not a satisfactory quartet, since 26771 is 5 vi depending on $p(-a)$, whilst p_a, p_b depend on $p(-a-b-\delta)$ and $p(-a+2b-\delta)$; on the complex basis this would mean that of the three terms involved the second would be displaced $+3b$ on the first, and the third $-(2b-\delta)$ on the second, and therefore quite inadmissible. In the absence of an established second separation it is not possible to use the own-multiple law to test if 829 is a real term difference on $p(-37\delta)$.

Unfortunately, the 487 is not sufficiently definite to test this. It is interesting to note, however, that if 26284 be corrected to make the d separation the normal 1412·70, the separation becomes 486·07. The 829·217 will go with this, but not 829·795 which is exact y larger. The mantissæ differences based on $p_1(-17\delta)$ are

$$24867 = 169\frac{3}{4}\delta - 1 ; 15012 = 102\frac{3}{4}\delta - 1 \quad \text{sum } 272\frac{1}{2}\delta - 2 ;$$

all exact within O.E. but showing no triplet effect, or perhaps indicating a triplet transference of about one own when the true displacement would be $170\delta, 102\frac{1}{2}\delta$. Note again $170 = 13^2 + 1 ; 102\frac{1}{2}\delta = 5(9^2 + 1)\delta_1$.

The 829 separation occurs in the Beals's quartets discussed later. Several are found also in the ultra-violet lines of Bloch, in connexion with others about 2046, which latter are very numerous. They should be summation lines, and in fact there seems some slight evidence for difference lines on the basis of the x limit. The following three examples, in which the ultra-violet summations are placed first, illustrate this statement. The first arrangement also illustrates a not uncommon phenomenon in spark spectra, where successive

repetitions of slightly differing configurations and meshes appear:—

L.

	2047·26	1,58259·45	833·07
4,60306·71 ⁽¹⁾	831·04	4,59475·67	2049·29
	683·53		6,57426·38
		683·62	
669·77	2046·59	3,59623·18	831·13
			4,58792·05
	829·45		
64546·94	2047·72	4,62499·22	
		49065·30	
	1,35631·39		

⁽¹⁾ Also with $-u'$ and $+e$ (see table iii.).

M.

	00, 63527·56
	828·72
	3, 64356·28
	49058·40 or ...60·11
	to 6y sat.
35806·73	2046·21
	6, 33760·52 (sat.) or
	2042·77 to 6y sat.
	(see 26 xii)

N.

	00, 67159·17
	829·19
00, 70034·38	2046·02
	00, 67988·36
	48062·70
	4, 30137·04

O.

	(sat.) 3, 30480·70	(894·16)	1n, 29580·05
		223·12	216·96
pa	3, 31670·28	1412·7	[30257·58] 894·47
		871·61	2n, 29363·11
pe	2, 33341·61	2042·93	6, 31298·68
	spc 371·72	spd 224·63	6R, 45141·01 (Wlf.)
	371·60: 223·1 = 5×74·3: 3×74·3 = 5:3		

Here 30480 is αA and an α -satelloid. Its red satellites at -10α , -15α give separations 895·29, 892·64. Stücklen gives four red. One at -12α would give 894·16. The 30257, though not observed, is substantiated by the observed sum of separations. The own test applied to the separations 371·61, 223·12 supports the basis of true term separations, for αp_c depends on $(3b) p_1 = 31376·89 = R/(1·86932)^2$.

The resulting mantissa differences are

$$11171 = 76\frac{1}{2}\delta - 8\cdot5; 6803 = 46\frac{1}{2}\delta + 7\cdot6 \quad \text{sum} = 123\delta - 0\cdot9,$$

showing both the systematic triplet variation and exact sum.

If 371 is $2X + (-b)$ on p , we look for about -50 on p_c or $+50$ on p_d , and find

$$\begin{array}{rcll}
 & 3, 31635\cdot97 & (1412\cdot84) & 8, 30221\cdot51(\text{sat.}) & \text{---} \\
 & 34\cdot31 & & (34\cdot45) & \\
 x p_d & 31670\cdot28 & 1412\cdot7 & [30257\cdot58] & 894\cdot47 \quad 2n, 29363\cdot11 \\
 \left\{ \begin{array}{l} 6, 33760\cdot53 (\text{sat.}) \\ 63\cdot48 \end{array} \right. & 50\cdot38 & & & \\
 & 2042\cdot82 & 1n, 31720\cdot66 & & \\
 & 50\cdot38 : 34\cdot31 = 1\cdot47 = \text{roughly } 5 : 3 & & &
 \end{array}$$

30221 is also an x -satelloid, the separations from a $3x$ satellite, but 31635 would be a forbidden line. Also the satelloid is $e.P_2.u$, and is too strong for this set. The evidence for a direct quartet depending on b is therefore weak.

In the preceding no attempt at a systematic discussion of quartet systems has been made. A few examples starting from observed ϕ -separations and some of the systems connected with the Shenstone lines only have been considered. In arranging these, starting from a ϕ -pair, the near lines giving the successive 1412, 894 separations have been sought, without reference to any theoretical ratios of the associated sets of separations (quartet A, of course, excepted). Nevertheless, these separations in all the examples show ratios of small integers with great exactness, $5:3-5:4-9:7:5$. Especially should it be noted that the p^4 ratio $5:3$ is shown by p_a, p_b for which there is independent evidence that they are fourfold terms, and the f^4 ratio $9:7:5$ is found in H with independent evidence from the Zeeman effect for at least the presence of F_{44}^4, F_{33}^4 . Also the abnormal ratio $5:4$ appears in both the related systems belonging to $m = 2, 3$ of the Rydberg $s(m)$ series. This, of course, is to be expected if we are dealing with real term differences, and considerable support is given to a real term theory by their fulfilling the own displacement law. But in several cases there is evidence that they are composite. In fact, it is difficult in at least the d^4 separations 2042, 1412, 894 to believe that they are other than almost pure linkages, although even here the proper d^4 ratios $7:5:3$ are in evidence. The question must be left open at present.

The quartets of Stücklen and of Beals.

12. We now pass to the consideration of the quartets which have been recently proposed: (1) two by Stücklen* in the violet, and (2) three with related intercombinations

* *Zeits. f. Phys.* 34, 562, 25.

by Beals*, independently later by Shenstone*, and implicitly by Sommer*. At a first glance, doubts as to their reality must be felt, for, as regards the quartets:—

1. The characters of the lines as arranged in their frames show complete dissimilarity between those in the central columns and those of the two extreme ones, as indeed was pointed out by Beals.

2. The separations involved seem excessive, and not only are they irregular, but they run even contrary to Landé's separation rules.

3. Many of these suggest at once the presence of compound links, as, *e.g.*, $636 = 3X$.

4. Each quartet consists essentially of lines of a single map; that is, the lines are link and collaterally related.

5. They have the fatal objection that negative terms are required. I have already in [I.] referred to these so-called negative terms. An electron describes a certain quantized orbit, which possesses a certain total energy value. Its "term" measures its energy-defect, *i.e.* the difference between the energy from infinity and the actual total energy. It is a measure of the work required to expel the electron out of the atom from that particular orbit, and it is this property which renders the determination of its exact value so important. It cannot be negative, or the electron would, so to say, expel itself. The reason why such negative values are given by certain writers is due to the fact that they are governed by the belief that all wave numbers are the difference of two terms only, and other phenomena are passed over, amongst which may be mentioned summation lines, and the possibility of an atom having two or more of its electrons raised to different levels and simultaneously falling in. This includes the case of links, every link being in fact due to a fall between two levels with the same k . For instance, if we find, say in Cu two lines at $n_1, n_2 = 30000, 30248$, the separation suggests that the lines are $p_1 - t_1, p_2 - t_1$, and that $30000 = p_1 - t_1$, producing a term $t_1 = 31524 - 30000 = 1524$. Suppose, now, a similar pair are found, 2041 ahead with $n_1 = 32041$. The two-term basis would give $t_1 = -517$, whereas the true value is $31524 + 2041 - t_1$ with $t_1 = 1524$ as before. In other words, if 1524 were a true term in the first case, it would remain so in the second, and no negative values be introduced. In all cases, repeated separations are due to term differences—*e.g.*, any link is a difference of two terms, and is so calculated. The error lies

* *Loc. cit.*

in the assumption that a wave number in all cases depends on two terms only. That the assumption is wrong is proved not only by the deduction of negative terms on that basis, but also from the actual existence of links, that is of separations, given by definite two-term differences in cases where neither of these terms can enter on a two-term line basis. Difficulties arising also from the existence of successive equal separations are specially considered below in the discussion of table iv.

Two remarks may be interpolated here:—(1) A link has hitherto been regarded as due to an electron fall between two near levels of the same azimuthal quality. But the presence of considerable multiples of the same link would on this explanation seem to require falls of several electrons between similar levels, a conception difficult to visualize. Another explanation might be that a rearrangement of electrons within the core would affect the values of the outer levels, and that such changes proceed by discrete steps, just as in displacement we find the discrete own steps. (2) The explanation of summation lines based on the simultaneous fall of two electrons in a doubly-ionized atom [I. p. 195] requires a very close simultaneity in independent events. This difficulty may be avoided by supposing that a singly-ionized atom is also highly excited, with an electron in one of its peripheral levels. The fall of an exterior electron might then precipitate the simultaneous fall of this peripheral electron. The actual peripheral level would be immaterial, provided its order is so high that successive values are practically equal. When they are lower the orbits may be sufficiently stable, so as not to be sensitive to the action of the entering one. If they are we should get displaced summation lines—unfortunately for our power of definite allocation.

The writers named—and indeed a large number of others—treat all wave numbers as given to one decimal place, whatever the accuracy of the observation, and they are satisfied with agreement in the various term-differences within a few units in the first decimal place, even when the accuracy of the measure is ten times or more larger. In many cases agreements are thus accepted where the more accurately observed would definitely exclude them. It would seem preferable always to give the wave number to a significant figure, one more than that of the observed wave-length. If not, when we come to additions or subtractions, both observation and calculation errors are altered in an unknown way. Then the results should be compared with possible O.E.

13. *Stücklen*.—The lines forming these quartets are of the same character, belonging practically all to her class i. of lines absorbed in the underwater spark. The corresponding separations are very closely equal, and in the first quartet (dp) they increase in roughly regular ratios 2 : 3 : 4 and 1 : 2 with the j values adopted by her. But these ratios belong to odd-fold systems, and there is the fatal objection that the j refer to a very unlikely combination. The 4, 3, 2, 1 belong uniquely to d^4 : 4, 3, 2 to f^3 , p^7 , or p^6 . The only possible conclusion would be that the quartet is an intercombination $d^4 p^6$, in which we should expect separations in the ratios 3 : 5 : 7 and 7 : 5, and these they decidedly are not. The quartet frame would be preserved by taking for j 1, 2, 3, 4 in place of 4, 3, 2, 1 and 1, 2, 3 of 4, 3, 2, in which case they would form a D^4 quartet, with a better intensity arrangement, but the separations now decrease with increasing j . If this last anomaly is accepted as possible, the arrangement must also be accepted as a perfect dp quartet. But I am inclined to think that where such an anomaly is found, it is a sign that composite separations are present, that the lines involve linkages, and that negative terms will be allocated by those who hold that all wave numbers are the differences of two terms. Her second quartet has such irregular separations that to me it appears unacceptable as a pure quartet; but this objection will not appeal to many recent writers. The first quartet is reproduced here in outline, the lines being represented by their intensities in (). Stücklen's j values are also entered, with those suggested above in ().

j	1 (4)	2 (3)	3 (2)	4 (1)
4 (1)			(2n) 724·11	(2)
			630·10	629·85
3 (2)	(6R) 574·64	(6R) 724·36	(1n) 574·71	(1n)*
	329·89	329·70		
2 (3)	(6R) 370·98	(2)† 574·73	(4R)	

The line denoted by *, 46748, has been added, as it reproduces the same separation 574 in a series, so that they cannot be pure term displacements. Also we find a similar series with 371, viz. † is followed by the line 44916 in her second quartet, separated by 371·62.

371. The region 44173 to 46250 of these quartets is included in fig. 1. The 371 occur also in Beals's quartet. They are produced in all cases by 2X links and a (b) displacement on $p(1)$. They are discussed together later. Here they are represented by the aa , bb , cc pairs in fig. 1 : 370·98— a_1a —does not show these intermediate lines, and is

probably not connected with the other 371. The fig. shows 5 chain representing it, $50 + v - X - X + 54$ or $v - 2X$, with (2*b*) on $p(1) = 370.86$. Whether real or not need not detain us. We consider in detail the first quartet only.

574.64; .73; .71 is the composite $e - 2Y_2 = 999.80 - 425.08 = 574.72$.

The intermediates are (unobserved indicated by a ●) :

44874-214.89	44659	997.11	45656-207.58	45449
44544-214.66	44330	999.80	● -210.41	45119
46173-210.23	45962	999.80	● -213.86	46748

724.11; .36. $724.2 = 574.72 + 149.48$ and (3*b*) on $p_2(1)$ shifts 149.43.

For intermediates we find

46079-208.88	45870-213.64	45656	997.20	●	149.43	46303
45449	1006.27	46455-205.87	46249-218.25	46031	142.21	46173

These show considerable displacements, but the X pairs form series inequalities, $X_2 + Y_1 + .04$, $2X_2 - .42$. In the first we get another example of 574.71.

630.10; 629.85. These differ by more than O.E. and by too much if real separations. They depend on X_1 , Y_1 , and are analogous to the 636 of Beals, which depend on X_2 , Y_2 (see p. 1211). Here $3X_1 = 629.64$; $3Y_1 = 630.63$; $2X_1 + Y_1 = 629.97$, etc. For intermediates

45449	207.58	45656	213.64	45870	208.88	46079
46173	207.95	●	207.96	46589	213.94	46806

We find a similar set in 25, 8*i*, 26, 27 of map II., viz. :—

31741.90	211.11	31953.01	206.48	32159.49	218.29	32372.78
						$= 630.88 = 3Y_1 + .25$

329.89; .70. Possibly a separation of two unrelated lines. The two values must necessarily be nearly equal, since the associated 574 are.

14. *The Beals quartets.* These are given as d, p ; d, f ; d, d quartets with common d^4 terms. They are reproduced below with the addition of certain intermediate lines in italics, which have been introduced for a purpose described below. Those enclosed in () in the third refer to a set which Beals attributed to an unknown term of probably f type. Their positions in the maps of [I.] are indicated either on the right of each line or collectively in the same column.

$Q_2 = F^4.$				
$\lambda.$	4.	3.	2.	1.
2		$1n, 20646$ $207\cdot6$ $2n, 20853$ $680\cdot0$ $2n, 21533$ $-148\cdot1$	$2n, 20853$ $636\cdot0$ $640\cdot5$ $636\cdot1$ $636\cdot22$	$212\cdot13$ $8, 21494S$ $887\cdot751$ $675\cdot62$ $739\cdot71$ $4, 22169$ $-148\cdot04$ $4n, 22021$
3	$2, 20840+$ $212\cdot20$ $2s, 21052$ $197\cdot30$	$544\cdot91$ $203\cdot84$ $4s, 21589$ $205\cdot44$	$207\cdot6$ $739\cdot5$ $203\cdot79$ $409\cdot28$	$212\cdot13$ $8, 21494S$ $887\cdot751$ $675\cdot62$ $739\cdot71$ $4, 22169$ $-148\cdot04$ $4n, 22021$
4	$6, 21249S$ $244\cdot277$	$545\cdot14$ $(-, 12, 11, 4 - -viii)$	$2n, 20853$ $636\cdot0$ $640\cdot5$ $636\cdot1$ $636\cdot22$	$212\cdot13$ $8, 21494S$ $887\cdot751$ $675\cdot62$ $739\cdot71$ $4, 22169$ $-148\cdot04$ $4n, 22021$
5	$8, 21494S$	$(-, 12, 11, 4 - -viii)$	$2n, 20853$ $636\cdot0$ $640\cdot5$ $636\cdot1$ $636\cdot22$	$212\cdot13$ $8, 21494S$ $887\cdot751$ $675\cdot62$ $739\cdot71$ $4, 22169$ $-148\cdot04$ $4n, 22021$

$$Q_3 = dd.$$

<i>i.</i>	4.	3.		2.	1.
1	(10, 11, 12 vii)	(17, 16, 15, 14 v, 29 vii)		$\left\{ \begin{array}{l} 1n, 18668 \quad 209\cdot7 \quad 2, 18878 \quad \quad 887\cdot65 \\ -50\cdot22 \\ 3s, 18618 \quad 211\cdot18 \quad 2s, 18829 \quad \quad 889\cdot85 \\ 371\cdot54 \quad 211\cdot18 \quad 210\cdot58 \quad 371\cdot548 \\ 2s, 18829 \quad 210\cdot58 \quad 0n, 19040 \\ 210\cdot58 \end{array} \right.$	$\left\{ \begin{array}{l} 2, 19556 * \\ -48\cdot02 \\ 1ds, 19508 \\ 2X_2 - \cdot 09 \\ 3, 19928 * \end{array} \right.$
2		$\begin{array}{l} 2n, 18404 \quad 214\cdot57 \quad 3s, 18618 \quad 211\cdot18 \quad 2s, 18829 \quad 210\cdot58 \\ -73\cdot20 \quad 636\cdot33 \\ 1ns, 18330 \quad 211\cdot19 \quad 2n, 18542 \quad \quad 639\cdot28 \\ 137\cdot83 \quad 211\cdot19 \end{array}$	$\left\{ \begin{array}{l} 210\cdot58 \\ 137\cdot41 \end{array} \right.$	$\left\{ \begin{array}{l} -70\cdot27 \\ 1s, 18970 \\ 207\cdot68 \end{array} \right.$	$\left\{ \begin{array}{l} 887\cdot66 \\ 887\cdot66 \end{array} \right.$
3 ⁽¹⁾	$\begin{array}{l} 3, 17997 + \quad 545\cdot24 \\ 680\cdot03 \end{array}$	$\begin{array}{l} 2n, 18542 \\ 680\cdot10 \end{array}$	$\begin{array}{l} 635\cdot76 \\ 209\cdot12 \quad 24s, 19643 \quad 214\cdot76 \quad (2n, 19858) \\ 210\cdot02 \quad 1n, 19434 \end{array}$	$\begin{array}{l} 680\cdot23 \\ 214\cdot76 \end{array}$	
8892·26	$\begin{array}{l} (2, 18677 +) \quad 545\cdot15 \\ 212\cdot23 \end{array}$	$\begin{array}{l} 892\cdot26 \quad (1n, 19222) \\ 212\cdot02 \end{array}$	$\begin{array}{l} 635\cdot90 \quad (-, 35 vii) \\ (-, 15 v, 31 vii) \end{array}$	$\begin{array}{l} 214\cdot76 \quad (2n, 19858) \\ 214\cdot76 \end{array}$	$\begin{array}{l} (-, 36, 37 vii) \\ (32, 31, 35, 39, 2, 3, 40 vii) \quad (39, 35, 38 vii) \end{array}$
4	4, 18889 * 544·96	1n, 19434			

(¹) Aretz measures for all three.

⁽¹⁾ Aretz measures for all three.

$$Q_1 = D^4.$$

4	3.	2.	1.
		3n, 22640 (4x)	887·88 4, 23528 *
		830·09	829·717
	6n, 22834 (3 viii) 636·7	2n, 23470 (13 x) } 887·51	4, 24358 *
		95·0	
	1095·6	1n, 23565 (7 x) } 1095·76	
		1000·76	
6, 23384 § S 545·028	4n, 23929 (12 x) 636·93	0n, 24566 (14 x) }	

Intercombination Lines (Beals).

d^2 .	2.	2042·87.	3.	s^2 .	f^2d^2	2.	2042·87	3.	s^2 .
	[]	„	2, 27816 †		4			6, 29950 S *	
			1095·357					(409)	
2	$\mathbf{x}p_a$	„	$\mathbf{y}p_a *$	$sp_a *$	3	6, 28317 S †	„	[]	
	829·795			829·889 ⁽¹⁾		739·64			
	$\mathbf{x}p_b *$			$sp_b §$	2	3, 29057 ⁽²⁾	„	[]	
					f^4				
			6, 32311 S †		3	$\mathbf{x}A †$	„	$\mathbf{y}A †$	
			892·334		p^2				
3	$\mathbf{x}B †$	„	$\mathbf{y}B †$		1	$\mathbf{x}p_f †$ ⁽³⁾	„	$\mathbf{y}p_f §$	$sp_f †$
	137·873		137·931		d^2				
2	$\mathbf{x}p_c §$	„	$\mathbf{y}p_c †$	$sp_c †$	3	$\mathbf{x}E *$	„	$\mathbf{y}E * §$	
	371·607			371·719		425·581		425·439	
1	$\mathbf{x}p_d †$			$sp_d †$	2	$\mathbf{x}p_g †$	„	$\mathbf{y}p_g$	$sp_g †$

$$3, 36104·93 † = d_1^2 d_1^4 \text{ (Beals) } = D_{22}^2(S_1).$$

(1) The value in table i. is 829·217. There are curious discrepancies in the measure here, especially in sp_b , $\lambda=2441$. The decimals given are '625 H.; '651 Krebs; 665 Hamm, with '64 K.R.; '67 E.H.; '65 E.V.; '67 Hup. It would almost appear as if H. had made a MS. mistake, writing 625 for 665. The W.N. given in table i. is from this '665, that entered here from '625. From the fact that the W.N. of the two differ by '67, or y , within possible errors, it is possible that the two sets belong to differently observed lines separated by y . The two θ values for p_a, p_b differ by exactly y .

(2) This comes in No. 5, p. 1165, and No. 11, table ii., whence it is seen that it has ϕ back, not forward as it should, and, moreover, has a true θ forward to a line which is "forbidden" if 29057 is $d^2 f^2$.

(3) This set and the two following were given by Beals as $d^2 d^4$. The allocations inserted are by S. and Sh., who agree.

For the sake of analogy with the others, the first, or D^4 , quartet is arranged with a same d term in the vertical columns in place of the usual D frame, in which the p -terms are in columns. S denotes a satelloid. Decimals in W.N. are omitted, but are given for the separations to three decimal places when the wave-lengths of both lines are given to three.

A glance at the list shows that each quartet consists practically of lines from a single map. Of the lines in the right column, depending on (434), and sustained, as we shall see, by their Z.P., only two occur on the maps. On the other hand, of those in the left—depending on (431)—and not well sustained by their Z.P., all but one occur in the maps. In the third quartet the two columns on the left both depend on map V., since those marked VII. belong to the centre of the map, and, as we already know, are not related to $D(2)$, but to the $\mathbf{y}-p_1$ connected by $\mathbf{y}-\mathbf{x}$ to map V. Since the lines in each quartet belong practically to one map, it is clear that the separations involved can be considered as compounded of the links and the a, b displacements indicated by these maps. A few of the quartet separations differ by more than observation errors. This points to different sources or to different displaced ρ terms on which the a, b displacements have to act. We must discuss the origin of these separations in some detail. But we will begin by considering some difficulties in the explanation of certain observed effects on the basis of the usual current assumption that all lines depend on the difference of two terms. The most important, perhaps, is the existence of successions of two or more equal separations (σ). If the lines are given by the difference of two terms, they are of the form $A-t_1, A-t_2, A-t_3$, where $t_2=t_1-\sigma, t_3=t_1-2\sigma$. Since any term is of the form $R/(\text{den.})^2$, where $\text{den.} = m + \text{definite function of } m \text{ and molecular and quantum constants}$, it would mean that the successive denominators must be so adjusted that the corresponding $R/(\text{den.})^2$ differ by equal amounts. One such case might be explained as a chance coincidence, but the large number of instances observed exclude this as a general explanation. Let us see how this is met in the present circumstances. For this purpose we select a few where the successive separations may be considered as equal within O.E. In other words no notice is taken of series inequalities or small displacements ordinarily occurring in linkage systems. Shenstone and Sommer are in general agreement as to the type of terms they adduce. As, however, this notation is extremely complex, those of Shenstone only are inserted below, and only differences between them indicated. Starting, from Shenstone's first list, assuming that the \mathbf{x}, \mathbf{y} are doublet d terms, and influenced by a common hypothesis, such general agreement is to be expected. In reproducing their allocations the usual term notation will be employed, different terms of the same ($r k j$) are represented by

Shenstone's prefix a, b, \dots , and barred and dashed letters by $(b), (c)$ inserted after the term symbol. The map places are also given; decimals in W.N. are omitted. *The term suffixes here are j values, contrary to the orthodox notation.*

TABLE IV.

(5, 2, 8 vi)	26771	680.11 ⁽¹⁾	27451	212.22	27664		
	$ad_3^4(c) - dp_3^4(c)$		$af_3^2 - dp_3^4(c)$		$ad_1^4(c) - dp_3^4(c)$	3.52	$af_3^2 - d. d_3^4$
				$(ad_3^4(c) - dd_3^4)$	27660	680.06	24340
(11, 3, 9 vi)	27189	212.27	27401	212.22	27613		
			$af_3^2 - cg_1^2$		$ad_1^4(c) - cg_4^4$		
(33, 31, 32 iv)	15371	692.50	16063	692.06	16755		
			$f_4^2(c) - d_3^4(c)$, Sommer				
(14, 18 vi)	$ap_3^2 - df_3^4(c)$	27425	999.73	28425	$af_3^2 - dg_3^4$		
(29, 28 vi)	$ad_3^2 - n_4$	28974	999.88	29974	$af_4^4 - cg_4^2$		
Som.	$d_3^2 - f_4^2(c)$				$f_4^4 - f_4^2(c)$ (all (b))		
	$P_2(1) = s^2 - p_1^2$	30535	999.96	29535	$af_3^4 - d_3$ (map i.)		
(37, 11, 15 vi)	$ap_2^2 - dd_3^4$	26189	999.74	27189	999.85	28189	$ad_1^4(c) - cs^2$
12, 16 vi)	$ap_2^2 - h_2(-f_3^4b)$	27319	999.08	23317.44	(y -sat.)	$md_2^2 - af_3^4$	
				8.52			
(10, 9, 4 iv)	$hd_2^2(c) - df_2^4(c)$	14625	680.76	15306	680.61	15986	$bf_1^2 - dg_1^4$
(17, 18 ii)	$md_2^2 - ad_2^4(c)$	31298	680.76	31979	$ap_3^4 - c_3$	(Som. $-f_3^2(b)$)	
(13, 12, 11, 10 viii)		20640	212.63	20853	680.04	21533	680.56 22214
			$af_3^4 \cdot cd_3^4$	The sum of the separations = $Y_2 + u' + u + 0$.			

				Sh.	Som.
(6, 7 iii)	32991	212.69	33203	$ap_2^4 - c_3^2, md_3^2 - ad_3^2$	$p_2^4 - p_1^4(c), d_3^4 - d_3^4(b)$
(12, 13 iii)	33341	212.63	33554	$md_3^2 - ad_2^4, ad_1^4 - p_1$	$d_3^2 - d_2^4(b), d_1^4(b) - f_3^2(b, c)$
(31, 32 vi)	29230	212.49	29442	$ap_2^2 - l_1, ap_1^2 - cp_2^2$	$p_2^2 - p_1^2(b), p_1^2 - s^2$

⁽¹⁾ In map VI., 2, 5, this separation is given as 680.26, and was based on Hasbach's measure 3734.23, whose other lines here are to three places of decimals. E. H. gives 3734.20, $n=26771.91$, sep.=680.06. H.'s spark line is enhanced to (3) and = ... 382. This is equal to $dn=1.12$, or 1.33 from E. H., mean 1.23, or one oon on the $p_1(1)$ term. Correcting his arc thus from his more accurate spark line thus displaced, $n=26771.82$, and the mean of this and of E. H. is taken.

From (1) we learn that 680.06 is due to $af_3^2 - ad_3^4(c)$ and 212.23 to $ad_4^4(c) - af_3^2$. In other words, lines separated by 680.06 must be represented by $Z - ad_4^4(c)$, $Z - af_3^2$. Every repetition of the same separation requires therefore a new term for Z . The additional set 27660 should be added to map VI. The remark as to new Z may be illustrated by the last fourteen examples of Sommer (p. 746 of his paper), associated with the θ separations. For another precisely similar case see footnote (2) on p. 1205.

- (2) The first line is not allocated. As we get here two successive X_2 separations, it is $ad_4^4(c) - af_3^2$ less than $af_3^2 - cg_4^2$, and so cannot be allocated as a pure difference line.
- (3) Two successive v seps, and same difficulty.
- (4, 5, 6) These are three sources for the e separations. They give $e = af_3^2 + df_3^4(c) - ap_2^2 - dg_3^4 = af_4^4 + n_4 - ad_3^2 - cg_4^2 = s^2 + d_3 - p_1^2 - af_3^4$, or two numerical relations between terms. (6) is the first link in map I., the whole of which seems quite incompatible with difference lines. With the allocations of Sh., 2i and 4i give $v = 692.11 = af_4^4 - dd_3^4 - (af_5^4 - dg_6^4)$, whilst 4, 5i give the P-doublet, $p_2^2 - p_1^2 = md_2^2 - ad_3^4(c) - (af_4^4 - dd_3^4)$.
- (7) Another succession of two e separations $e - .06$ and $e + .05$, making with (4, 5, 6) a third numerical relation. Naturally the middle line has received no allocation.
- (8) Another e giving with the others a fourth numerical relation. The last is a y -satelloid with satellites at $-4y, \delta_1$ on $p_1, +2y, +4y$. The 999.08 is measured to the first violet satellite. To a $3y$ satellite the sep. would be $999.71 = e - .09$.
- (9) gives two successive u with no allocation for the central line.
- (10) gives another explanation for u and with (9) compels another numerical relation between terms.
- (11) has only an allocation for the first line.

The three examples in (12) again require four terms to express the value of Y_2 , and with (11) give a fresh set of four numerical relations between terms.

Similar difficulties appear from the general constitution of the second quartet. With a new line $2n, 21533.62$ they appear to contain two parallel doublet d sets separated by 636, which may be written thus:—

$$\begin{array}{rcl}
 4n, 22021.73 & & 6n, 21385.51 \\
 148.04 & & 148.1 \\
 4, 22169.77 & 887.75 & 4n, 21282.02 \quad \left| \quad 636.22 \quad \left| \quad 2n, 21533.62 \quad 887.6 \quad 1n, 20646.0
 \end{array}$$

The allocations are:—

$$\begin{array}{ll}
 af_3^4 - cd_2^4 & af_3^4 - cd_3^4 \\
 af_2^4 - cd_1^4, af_2^4 - cd_2^4 & \text{none} \quad af_2^4 - cd_3^4
 \end{array}$$

The left hand gives $887 = cd_2^4 - cd_1^4$, so that 21533 would be $af_2^4 + cd_2^4 - cd_1^4 - cd_3^4$, or not a difference line. This

quartet contains also two satelloids, in one of which, 21494, the first violet satellite, shows 3 u back to 19454.

Another kind of difficulty on the term basis may be illustrated from the chains in map XIII., connected with (18). No. (19) is Beals's $d_2^2 - f_2^4$, and is accepted by Sommer. The latter recognises the θ separation to (17), and is obliged to give it $s^2 - f_2^4$ or $k=1 \rightarrow 4$. At the same time (18) is ϕ behind (19), instead of ahead, so that this cannot enter by the allotted $\phi = d_3^2 - d_2^2$. It is given $f_4^2 - f_5^4$, the second f barred, a new term. (22) is $p_2^2 - s^3 d_2^3$, but here 2041.49 is not ϕ , but connected with 3 u . In any case, a new numerical relation between terms results.

15. We now return to the more detailed discussion of the constitution of the separations exhibited in the Beals quartets, and concurrently to consider the evidence from the Zeeman effect. To assist in this certain intermediate lines have been inserted in italics in the above reproduction of these quartets. They serve to indicate the actual presence of links and displacements which go to the constitution of the separations. We begin with the d -separations common to all the quartets.

887. Obs. 887.88, .51, — 887.751, — 887.65, .66. There is also the 887.6 given above. The (432) lines are very nebulous, so that all these values may be equal within O.E. It seems a composite of two diminished u and X links. The nature of the diminution is indicated in the second quartet, where the intermediate is a y -satelloid, in which Hasbach gives two red and two violet satellites and Stücklen states that there are four red and six violet. The set is (9, 7, 8 viii). Hasbach's readings give

88.75, (89.59) 90.20, (91.87) 21494.15, 96.00, 97.98 (−9 y , −7 y , +3 y , +7 y)
22169.77 680.18 | −4 y | 209.85 21282.02

If we suppose two extra satellites at −8 y , −4 y , their wave numbers are as entered in brackets and their separation from the two quartet lines are within O.E. of u' and X_1 , and the observed diminution is the 4 y . In fact

$$u' + X_1 - 4y = 887.66.$$

We get a similar indication, clearly seen in map VIII. 11, 12, 13, 13 a in the new separation above by the existence of another line 20640.95. Thus

21533.6 680.0 20853.6 212.7 20640.95 (13 viii)

50

207.6 20646.0

It is instructive to note that 20640 has been observed by *Phil. Mag.* S. 7. Vol. 4. No. 25. *Suppl.* Nov. 1927. 4 I

E.H. alone and 20646.0 by Hasbach alone in the arc, but .42 by E.H. in the spark, or y within O.E., whilst E.H. give separation = 5.47 or $9y$. It suggests that these two are of satelloidal nature. The 20640 gives $u' + Y_2$, and 20646 gives $X_1 - 4y = 209.88 - 2.28 = 207.6$, the complete separation being again $u' + X_1 - 4y$. Although these are the only indications directly of the presence of the y , the diminished u and X are also present in the third quartet between 18668 and 19556, as well as in the intermediates shown in this quartet. Other illustrations are found in (44, 43, 46 vi) and in the third quartet round 19177, viz. :—

$$208.63 + 678.93 = 887.56; \quad 207.68 + 680.23 = 887.91$$

In the former the first line is allocated to $d_3^2(b) - d_2^2$, and since the 887 is due to $d_2^4 - d_1^4$, the last line is expressed by the sum of these; i. e., by four terms. In the latter no allocation is given for the first line, probably because being a spark line it was not considered. That, however, is really a support of their system, as, taking their formula for the last line, that for this line should be $af_3^2 - cd_1^4$, and consequently be "forbidden." As another example take the following two lines with the allocations as given :—

$$af_4^4 - dd_4^4 \quad 4, 30114.65 \quad 887.52 \quad 3, 31002.17 \quad af_2^4 - df_3^4$$

The difference of these expressions (four terms) must equal $cd_2^4 - cd_1^4$; another example of a numerical relation between terms. The constitution suggested, $u + X - ny$, is, however, quite a common one. Indeed, if we examine the satelloids we shall find a very considerable proportion have relations of this kind. As this particular kind of modification is an essential in the explanation of the complex form of the 887 separation, the examples are here given.

Sat. 2 (9, 7, 8 viii) in df above.

Sat. 4 (50, 49, 51 ii) 26861 **680.12** 27541 **212.23** 27754.17 (6.39) $u' + X_2 + .03$ and $+4y -$

Sat. 6 (42, 47, 26 vi) 29267.10 **679.94** ($-7x$) 29950.82 ($-13x$) **209.83** 30153.63;

$$886.53 = u' + X_1 - 6y -$$

The satelloid seems a mixed x, y . It has satellites at $-3y, -4y, -10x, +2x, +3x$. The separations here given are those for supposed satellites at $-7x, -13x$. In addition 29057.08 **210.11** behind 29267 gives with 29950 a separation **893.74** $= u' + Y_2 + 2y + 0$.

Sat. 15 (32, 31, 30 ii) 31953 **680.83** 32633 (8) **207.79** 32841; **888.62** = $+Y_1 - 3y +$

H gives single violet sat. Stücklen states 6r, 3v.

Sat. 16 (2, 1, 3 iii) 32037 **212.18** 32249 **677.83** 32927.38, 2972, 3026; **890.01** $= u' + X_1 +$

Stücklen gives $8r$, $6v$.

For examples with $n=0$ see under 892 (p. 1217).

636. Obs. $636\cdot7$; $\cdot93\uparrow$ — $636\cdot0$; $22\uparrow$ — $636\cdot33\uparrow$; $635\cdot76\uparrow$ — $635\cdot90\uparrow$ with $636\cdot1$ in the new example of the two triplets. Those marked \uparrow are from moderately good measures. It is clear that they cannot all be equal, so that the allocation of immutable term systems is not applicable. The value suggests at once the constitution $3X$. Thus $3X_2=636\cdot81$, within O.E. of two sets, $3X_2-y=636\cdot24$, $3X_2-2y=635\cdot67$ meet the others, but there is no satelloid evidence for the introduction of y . The intermediate components are indicated in the third quartet, but not in the first, whilst other instances of the 636 occur in the intermediates. We find similar successions in map VII. nos. 25, 29, 31, 35, 29.

18193 210 63—214 56—211 08—210 64 19040

The sums of the first and last three are respectively $636\cdot27$, $636\cdot33$. We have already found examples of $3X_1$ in Stücklen's quartets.

545. Obs. $545\cdot028$ — $544\cdot91$; $5\cdot14$ — $545\cdot24$; $\cdot96$ — $545\cdot15$. These can be equal within O.E. It is approximately met by $v=692\cdot08$ and a $3b$ displacement on a p term, *e.g.* ($\pm 3b$) on p_1 shifting $-147\cdot64$, $148\cdot74$, and there seem indications of this in Q_2 , Q_3 , viz. :—

(14, 11, 4 viii)	20840	693 2	21533	-148 1	21385	545 14
(10, 9 vii, 17 v)	18889	691 83	19581	-146 87	19434	544 96

If we accept the map VIII. 21385 in Q_2 depends on $(-\delta_1)S(3)$ or on $+p_1$, whilst 19581 is $y-p_1$. As $(-3b)$ on p_1 shifts $148\cdot74$, $v+(-3b)$ on p_1 in both examples gives $692\cdot08-148\cdot74=543\cdot34$ or one unit less $=544\cdot58$. In other words, although the constitutions of the lines in the two cases are quite different, the $-3b$ displacement produces the same effect. As, however, in the new discussion of map VIII. below the 693 has been treated as a false link, this explanation of the origin of 545 can only be accepted as possible. I am inclined to think that this separation is a chance difference, repeated because all the other separations adduced in the quartet are equal amongst themselves.

We take now the separations of the current terms in the three quartets, including also the corresponding values in Beals's intercombination sets (adopted also by S., Sh.). After

the consideration of the separations of each quartet, the discussion of the Zeeman effect will follow.

$$Q_1 = D^4.$$

829. Obs. 829·717; 830·09—829·795; ·889* or ·217 (intercomb.). The intercombination lines are Shenstone's p_a , p_b considered on p. 1181, where it was found that the separations were met by $u + (3b)$ on $p_1(-a-b-\delta)$, giving 829·60. In the quartet the line 22640·64† is $2e.X_1.D_{22}(3)(-4\delta) + \cdot 02$, and the two sets of lines are connected by the 887 or $u' + X_1 - 4y$, giving evidence of the entry of y . In this case $(-3b)$ on p_2 shifts 150·50 and $u' + (-3b)$ on p_2 gives 830·56, within O.E. of the 830·09.

We find a similar example in association with the first of the sets adduced in connexion with the discussion of the origin of 545, by the addition of a u link to the middle line (4, 11, 10 viii).

$$u_1(-\delta_1) S_1(3), \quad 21385 \quad 148 \cdot 10 \quad 21533 \quad 680 \cdot 56 \quad 22214 \quad 828 \cdot 68$$

Here $u' + (-3b)$ on p_1 gives 828·80. This is specially interesting as showing how the similar but slightly different values observed arise from the same displacement on differently modified p terms.

1095. Obs. 1095·76; ·6—abs. 1095·357. The intermediate placed in the quartet suggests that the separation is e with $2b$ displacement. On the $D_2(3)$ basis of the map, 23470 contains $(-3b)p_2$ and $(-2b)$ on this shifts 100·93 or $e + (-2b)$ on $(-3b)p_2 = 1100·73$ or with $(-2b + \delta) = 1095·73$.

On the $p_a = -p_1(-a-b-\delta)$ basis $(+2b)$ shifts 99·47 and $\text{sep.} = 1099·27$.

Note. $(-a+b-\delta) = -17\delta = -(4^2+1)\delta$ in association with $-(6^2+1)\delta$ of p_a (see discussion of p_a (p. 1181)).

* See note (1) to intercombination list.

† This line is interesting since Hasbach gives the spark representative as less by $d\lambda = \cdot 67$ or $n = 3\cdot 44$ larger and equal therefore to $2e.X_1.D_{21}(3)(-4\delta)$; in other words, the spark line appears as the analogue to the "forbidden" D_{21} . The shifts at disposal are so small (δ shift on $d(3) = \cdot 5077$) that we can get no reliable evidence for any precise allocation, but with the above allocation we find a summation line by E.V. at $\lambda = 1$, 2740·07 $n = 36485\cdot 84$ giving a mean limit 29563·24 with 22640·64. The calculated limit $2e.X_1p_2 = 3172\cdot 97 - 1999\cdot 60 - 209\cdot 88 = 29563\cdot 49$, and so far sustains the allocation.

The Z.P.

The 1st col. gives n , the 2nd the line type with quartic index omitted, the 3rd the theoretic Z.P., and the 4th the obs. H. denotes Hartmann.

23528	D_{34}^4*	1·33/1·33	1·30/1·30 B.; 1·31/1·31 S.
24358	D_{44}^4*	·87/·87, 2·60	·81/·81, 2·60 B. ·87/·87, 2·62 S.
23384	$D_{11}^4\S$	09 —/1·00-----	0/1·18 B. 0/1·13 S.; 0/1·16 H.

The first two must be taken quite definitely as established. These are the two lines which appear in no map, as in this case they should not. For the third the most that can be said is that it is just possible if 1·18 is a merge. But if so, we should expect the observed and components to show as a broad band. Really the observed points directly to a Z.P.=0/1·20, of which there are several cases, *e.g.* $d_1^2d_1^2$; $d_1^2d_3^4$; $d_3^4d_3^4$. D_{11}^2 , F_{11}^2 , F_{11}^4 might give merges also like that supposed for D_{11}^4 . The allocation appears to me improbable, but I have marked it §.

$$Q_2 = F^4.$$

739. Obs. 739·71; 9·5—739·64; abs. This is the 887·75—148, *i.e.* a (3*b*) on a p (1) term. If we accept map VIII., the set depends on $S_1(3)$, and 22021 is $u.S_1.3Y_2-.05$, on which (—3*b*) shifts 148·74 (see rediscussion of VIII. at end) and $u + X_1 - 4y + (-3b) = 739·49$. As 21385 is only linked to 22021, its p sequent is the same, and the (—3*b*) displacement has the same shift. In the intercombination the $j = 3 \rightarrow 3$, 2 are absent, whilst $2 \rightarrow 3$, 2 are 6, 28317·435 S. (16 vi) and 3, 29057·08 (43 vi) with anomalous orders of intensities. If the allocations in map VI. are accepted, the formulæ may be written

$$28317, 2Y_2.2e.u P_1(-b) v-6y-.03$$

$$29037, 2Y_2.2e.v P_1.2v-10y+.34$$

The difference is seen at once as $v + (-b)$ on $p_1-4y+.37$ ($d\lambda=.04$). The reality is illustrated by an intermediate line 28366·83 (17 vi) separated $690·25 = v-3y-.08$ and 49·40. The origin of the separation is thus $v + (-b)$ on p_1-4y , different from the former, as might be expected from the different nature of the terms involved. It may be noted also that the 2042 separations are wanting in this intercombination set. In fact 29057 has ϕ back and a θ which would require a forbidden $s-f$.

409. Obs. 409·50 ; 9·28—no intercombination. The 409·50 is accurate to the last decimal. Although the lines for 409·28 are nebulous, H. and K.R. both agree, and E.H. make it ·04 less and E.V. ·09 greater. They are therefore clearly different. We find intermediate spark lines for both, which, since $197 = 4 \times 49$, indicate the composition $X + (4b)$ on a p . Accepting map VIII., 20480 depends on $(b)S_1$, i. e. on $(b)p_1$, and $(-4b)$ on this shifts 198·05 or another one 199·29, so that $Y_1 + (-4b - \delta_1)$ on $(b)p_1 = 409·50$.

For the second set however 21385, p_1 enters as $(-\delta_1)p_1$, on which $(-4b)$ shifts 198·56 and

$$Y_1 + (-4b) \text{ on } (-\delta_1)p_1 + y = 409·34.$$

The Z.P.

22169 ⁽¹⁾ F ₄₄ ^{4*}	·20/·20 ; 60	·23/·23, ·64 B ; ·21/·45 S.
21794 F ₂₂ ^{4§}	·07 --- / ·90 - - - - -	0/88 S. ; 0/·97 Sh.
21494 ⁽²⁾ F ₁₁ ^{4§}	·05, --- / 1·00 - - - - -	0/1·20 B. ; 0/1·30 S. ; 0/1·09 H.
21249 ⁽²⁾	·09, --- ·67 / - - - 1·33 - - -	·64/1·40 B. ; ·65/1·42 ; 4 comp. H.
20840 F ₁₃ ^{4†}	·20, --- / ·43 - - - - 2·43	0/2·20 B. ; 0/2·05 S.

⁽¹⁾ Lüttig states that H. has observed the Z.P. for $\lambda = 4507·6$ as a very faint normal triplet; but this must be in error for 4509·60 (i. e. $n = 22169$), since 4507 is a very broad and weak line whose Z.P. could certainly not have been observed. Indeed, Kayser's 'Handbuch' notes 4509, and not 4507, as having had its Z.P. determined.

⁽²⁾ "Higher splitting not excluded." (H.)

F₄₄ must be regarded as established.

F₂₂ is possible but not absolute, since a very considerable number of allocations meet the observed equally well. In fact F₂₂² is better, requiring ·03—/·77, — ·94 with G₂₂² as good ;—marked §.

F₁₁. H alone supports the allocation. It appears rather to belong to one of the 0/1·20 ;—marked §.

F₁₂. Possible, but the symmetric σ pattern should require the measure 1·33, even if they merge. The Z.P. for S₂² or P₂² are as good, ·67/1·33, but D₂₃⁴ = ·27, ·80/—, 1·47,—is the nearest ;—marked §.

F₁₃. With a component separation of ·40 ($d\lambda = \cdot 1$), 2·43 should stand by itself without a merge, and the ω should have been seen as two. The pattern of S. is that for p_1^2, p_1^4 , viz. 13,—/1·20, — 2·00 ;—marked †.

The evidence that the scheme of lines in Q_2 represents an F quartet is very slight. The remarks on p. 1208 make its reality very doubtful, and the corresponding intercombination are defective. The evidence from the Zeeman effect is weak, and the direct evidence for F_{44}^4 only points to the existence of an F quartet which has not yet been allocated.

$$Q_3 = d^4 d^4.$$

371. Obs. 371·548; 1·54—371·607; 1·719 (inter.). The intermediate lines shown in the quartet and (7, 8) below for the intercombination indicate that this separation is 2X with $-b$ displacement on p . Map VII. gives both 18668 and 19556 as depending on $(b)D_2(2)$, *i.e.* on $(b)p_2$, and b on this shifts by $-49·81$ or $b-\delta_1$ by $-48·56$. Thus $X_1 + Y_1 + (b-\delta_1)$ displ. gives 371·53. The point here is that the separation is met by 2X links and b on $(b)p_2$ whether that just given is real or not. Since the first and second columns are only link related, the same explanation holds for the first as for the second. The intercombinations have already been discussed under $p_c p_d$. But there is this difference, that while here p_1 enters + in D_2 , it enters as $-p_1$ in $p_o p_d$, and the composition is $2Y_1 + (-b)$ on $P_1(3b) = 371·32$.

There are very large numbers of instances of this $2X + (b)$ displ. with actual separations varying according to the particular X links and the terms in which the (b) displacement is taken. The following are instances:—

1, 376·96		2, 373·5 (three arrangements)	
17960·71s		19484·70s	
210·86	209·28	209·28	-50·46
17751·85	19693·98	19693·98	19434·24
213·61	209·84	-50·62	209·12
17538·24y p_1	19903·82	19643·36s	19643·36s
-47·51	-45·6	214·8	214·8
17585·75s		19858·2	
3, 367·34		4, 367·08	5, 371·40
31741·90		33048·34	45229·81
211·11		-57·34	217·74
31953·01		32991·00(6 iii, 37 xii)	45447·55
(208·25) 206·48		212·68	209·22
(61·28) 32159·47(8 i)S		33203·68	45656·77
(-52·04) -50·25		211·75	-55·56
32109·24		33415·42	45601·21

6, 372·65	7, 371·607	8, 371·719
45449·19	31298·6778 $\times p_c$	44544·659 sp_c
207·58		-54·40
45656·77	2×210·99	44490·26
213·64		214·14
45870·41	31720·66	44704·40
-48·57	-50·38	211·97
45821·84	31670·284 $\times p_d$	44916·378 sp_d

There are several also with the (*b*) displacement added. Thus, in vi, 11, 3, 9, 8 and 11, 3, 2, 8 give **212·26 + 212·23 + 50·36** and **212·26 + 50·36 + 212·23**, and in vii, 25, 29, 31, 32 give **210·56 + 214·63 + 50·53**.

The continued repetition of these distorted X and (*b*) in regions where the spectrum is not crowded, shows that they form sets really associated with current distortion. Nos. 5, 6, 8 are *bb*, *cc*, *aa* in fig. 1 and 7, 8 refer to Beals's intercombination sets.

137. Obs. 137·83; 41—137·873; 931. For the first two the maps show 3 vii—39 vii and 29 vii—15 v. The 3 vii is very doubtful. The two must be of the same type since they are merely linked by 3X. The intermediates inserted in italics in the quartet seem to indicate $X \rightarrow (a-b)$ on a p term. A $p_1(1)$ term would give for $X_2 + (a-b)p_1(1) = 212·54 - 75·15 = 137·39$, and $Y_2 + \dots = 137·66$. In the "intercombination" pair the origin appears to be different. It was discussed above in connexion with the interpretation of x_A etc. (p. 1178). It was there found as a (*3b*) displacement and an interchange of u, v links.

892. Obs. 892·26; 26—892·334. These are given by the two links $u' + X_2 = 892·33$. Indeed the whole set of separations 887, 894, 892 and others near appear to belong to a single type $X + u + ny$ where n is a positive or negative integer. There are very many examples of the Rydberg separations remarkable for their exact agreement or exact within y -multiples. They and the 680, 212 are met by B., Sh., and S. by differences of three terms of the type (43'3), (243), (43'4), say, d_2^4, f_3^2, d_1^4 . A set of successive 680, 212 are produced by $d_2^4 - Z, f_3^2 - Z, d_1^4 - Z$, or successive 212, 680 by $Z - d_1^4$ etc., where Z denotes some common term for that set, and for other sets a new term Z has to be introduced. The following list contains the majority of sets. Where they have allocated no terms the wave number is in italics. The normal large separation is taken as $892·33 = R$. The last column on the right gives the

allocation of the above Z by Shenstone. An asterisk refers to the succeeding discussion.

1. (12, 11, 10 vii)	17997	$u'-.02$	18677	$X_2-.04$	18889	$R-.06$	e^4D_4
2. (15, 16, 17 v)	18541	$u'+.16$	19222	$X_2-.21$	19434	$R-.05$	e^4D_3
3. 31, 35, 36 viii)	18618	$X_2-2y-.05$	18829	$u'-2y-.14$	19508	$R-4y-.19$	
4. (13, 12, 11 viii)	20640	2127	20853	6800	21533	8927	
5. (6, 3, 9 vi)	26721	$u'+.05$	27401	$X_2-.04$	27613	$R+.01$	e^4G_1
		$X_1-3y-.03$	26932	$u'+3y+.04$			*
6. (5, 2, 8 vi)	26771	$u'+.04$	27451	$X_2-.09$	27664	R	d^4P_3
7. (50, 49, 51 vi)	26861	$u'+.06$	27541	$X_2-.04$	27754(S4)	$R+.02$	d^4D_4
{	27686	$u'-.02$	28365	$X_2-.01$	28579	$R-.03$	d^4F_4
	28579	$X_2+2y+.0$	28792	$u'+.05$	29472	$R+2y+.05$	*
9. (21, 24, 25 vi)	29472	681.02	30153	210.71	39364	$R-y-.03$	*
10. (25, 26, 26a vi)	31741	$X_2-2y-.02$	31953	$u'+y+.20$	32633(S15)	$R-y+.18$	*
11. (32, 31, 30 ii)	32037	$X_2-.10$	32249	677.835	32927.382 } (S16)		*
12. (2, 1, 3 iii)				$u'+.11$	9.72	$R+.01$	m^2D_3
{	32311(S13)	$X_2-.04$	32523(S14)	$u'+.05$	33203	R	*
		$u'-y+.16$	32991	$X_2+y-.16$			
14. (5, 7, 17 iii)	32523(S14)	$u'+.05$	33203	$X_2-y+.04$	33415	$R-y+.09$	*
15.	45141	$u'+.19$	45821	$X_1-.38$	46031	$u'+X_1-.19$	*
16. (in v)	D_{11}	212.55	(14) 211.19	15 680.04	16 212.23	17	
		(3) 678.40	889.59	891.29	892.27		
		890.95					

In the first place we notice that the satelloids occur in Nos. 7, 11...14, and that where the separations vary from their normal values outside their O.E., the changes are met by the ubiquitous y -multiples, remarkable in their completeness. In one case (12) the satellite is present, and the 892.35 is exact within .01. This effect is important as showing that any small variations from normal values arise from y -modifications and are not due to new terms.

3. The y rule shows that this belongs to the system. No allocations have been given, but on their basis a new Z term should be introduced.
4. The separations are correct within O.E. and a second new Z is required.
5. This gives a mesh, the line 26932 established by the very exact y relations. Sh. and S. disagree in its allocation with 232-211 and 232-421 respectively. The separations of the mesh are 680.11, 212.23 and 210.53, 681.81. The upper set are $d_2^4, f_3^2, d_1^4 - Z$. To represent the lower set requires $Z' - d_1^4, Z' - f_3^2, Z' - d_2^4$, and it is impossible for two such sets to co-exist*. (13) is another similar case, but is not so decisive, for the variation from a y -multiple in the 32991 ($dn=.17, d\lambda=.016$) is close to its possible O.E. Sh. and S. again disagree, giving respectively 422-211 and 422-421. 8, 9, 10 give a double continuation, established as real by the y -relation, and quite impossible to explain on the term basis. Consequently both Sh. and S. exclude the $X_2 + 2y + 0$, and the 681.02 as representing real separations. Again they disagree in allocations, viz. :—

28792	433— h_2	433—443
29472	243— h_2	243—443
30153	not allocated.	
30364	443—422	443—412

here h_2 means some term whose $j=2$.

11. The line 32633 is given as a satelloid, but its single "satellite" given by H. is probably a two own displacement on p (1). Stücklen gives $6r$ and $5v$. It is

* In passing it may be noted that seps. $a, b; b', a'$ in parallel cannot be produced by difference terms of the above form. If, however, the terms involved are related, as, e.g., in a diffuse triplet d_1, d_2, d_3 , they are successive displacements on one, say, $t, t(-\alpha), t(-\alpha-\beta)$. The separations a, b are $t(-\alpha)-t, t(-\alpha-\beta)-t(-\alpha)$ and the b', a' are $t(-\beta)-t, t(-\alpha-\beta)-t(-\beta)$, but in this case the mesh is not exact. But the deviation must be calculable. This kind of inequality is seen in the example. Whether (5) conforms or not is a question of the unknown Z . The y deviation points to its not being of this nature.

Shenstone's x_{pf} of his first paper. The allocations are 443-443 (i. e. f_2f_2), 422-433, 232-222, i. e. neither accepts the lines as an R set.

12. Here the observed satellite gives exact R. The set must be accepted and requires a third new Z. Sh. and S. disagree for the first with 422-453, 422-432, and give 423-434, 232-232 for the others.
- 13, 14. See under 5. Also here we find a continuation, established by the y rule and the presence of two sateloids, 32523 is an x set. Expressed in x the seps. are $u'-x+\cdot13$, $X_2+x-\cdot13$, and $X_2+x+\cdot01$. Naturally no allocation is given for 33415.
15. I have included this although not of the R type, but the analogous $u'+X_1$. Piña de Rubies has observed 48073·77, 2042·43 ahead of 46031, a clear $y-x$ separation. S. has recognized this and consequently allocated 232- e_3 , 233- e_2 , where e is some $j=2$ term. The others are 233-222, 211-221.

We have this $y-x$ link back from 18541 in (2), viz. 2043·39. If real, the link hypothesis requires a 233 term in 18541 given as 433-433. Also a forward 2041·97 from 27664 in (6), but here it is a clear $3u$ link. If the ϕ sep. is taken 27664 should contain the 223 term (given 423-434).

16. (3, 14) are spark lines by E.V. If they are each corrected by $\cdot10(d\lambda=-\cdot04)$ the four sets become $R-4y+0$, $R-5y+01$, $R-2y$, $R-\cdot06$.

The Z.P.

1. 19556	$d_1d_1*\S$	not affected	not affected B. & S.
2. 19928	d_1d_3*	$\cdot60/\cdot60$, 1·80	$\cdot55/\cdot55$, $1\cdot63$ B.; $\cdot54/54$, $1\cdot63$ S.
3. 18889	d_1d_1*	$0/1\cdot43$	$0/1\cdot44$ B.; $0/1\cdot42$ S.
4. 17997	$d_1d_2^\dagger$	·03 , --/-- -- -- 1·57	$0/1\cdot88$ B.

1. The allocation is met, but cannot be uniquely proved—marked * \S .
2. The observations could be explained by an error of 1/12th in measuring the field, but the agreement by different observers puts this aside. Some disturbing effect (linkage?) has evidently occurred in the line itself—marked *.
3. This is a good agreement, but d_2d_2 has $0/1\cdot37$. The line appears in 10 vii as $y-p_1-v=D_{11}^4-v+\cdot24$, but the Z.P. does not agree with D_{11}^4 . Either the link is not real or the link has affected the Z.P.

4. This is definitely wrong. It is nearer $p_2^4 p_2^4$ with $0/1\cdot73$; $d_1^2 d_1^4$ with $\cdot11 - - / - - - - 2\cdot00$; or $d_1^2 d_2^2$ with $\cdot20, - / - - 1\cdot80$ —marked †.

Z.P. Intercombination (Beals).

The majority has been discussed above as entering in Shenstone's first list. Here follow the remainder :—

1.	27816	$p_1^4 d_1^2 \dagger$	$\cdot20, \cdot60, 1\cdot00 / - - 1\cdot40 - -$	B. gives $\cdot99$, presumably $\cdot99/\cdot99$.
2.	29950	$d_1^2 f_2^4 *$	$\cdot02 - - / 1\cdot14 - - - - 1\cdot33$	$0/1\cdot26$ B.; $0/1\cdot28$ S.
3.	28317	$d_2^2 f_3^4 \dagger$	$\cdot12 - / \cdot68 - - 1\cdot39$	$0/1\cdot20$ B.; $0/1\cdot14$ S.
4.	29057	$d_2^2 f_4^2 *$	$\cdot20, \cdot60 / \cdot20, \cdot60, 1\cdot00$	B. gives $\cdot60$, presumably $\cdot60/\cdot60$.
5.	32311	$d_1^2 \bar{a}_1^4 \dagger$	$\cdot11, - - / \cdot86 - - - - 2\cdot00$	$0/1\cdot78$ B.; $0/1\cdot7$ Sh.
6.	18677	$d_1^4 f_2^2 \dagger$	$\cdot28 - - / 0 - - - - 2\cdot86$	$0/2\cdot14$ B.; $0/2\cdot15$ S.
7.	19222	$d_2^4 f_2^2 \dagger$	$\cdot26 - 1\cdot29 / - - 1\cdot11 - -$	$0/\cdot73$ S.
8.	36104	see note		$0/\cdot96$ B.

1. The σ forbids the allocation. This definitely rules out 1095 as a quartic p separation.
2. The components are too close to have been observed, but a merge at $1\cdot26$ would mean that all the six σ components are practically of equal intensity. It may be noted that the line $d_1^2 f_3^4 (j=3 \rightarrow 3)$, which should have been at least of the same intensity as this strong line, is not observed. $f_1^2 g_2^4$ with $\cdot01 - - - / 1\cdot07 - - - - - 1\cdot27$ is exact and the only possible even fold combination up to $k=5$.
3. The σ negative the allocation. It would be one of the many $0/1\cdot20$.
4. Is good if $\cdot60$ means $60/60$.
5. If this is accepted it would mean the falling out of the stronger σ component. The Z.P. points to $f_1^4 f_2^4$ with $\cdot05 - - - / - - - - - 1\cdot67$, or to $f_2^4 f_2^4$ with $\cdot10 - - / - - - - - 1\cdot76$ exact.
6. Both π and σ forbid this. $D_{13}^4, \cdot20, \cdot60 / - - - 2\cdot20$ is better but not satisfactory, or $f_1^2 f_1^4$ or $f_2^2 f_2^4$ (best) $= \cdot19 - - / - - - - - 2\cdot19$. But it is probably a non-Landé pattern.
7. Quite inadmissible.
8. Given by B. as $d_1^2 d_1^4 (\cdot11 - - / \cdot86 - - - - 2)$ by S. as $D_{22}^2 (\cdot07/\cdot73, \cdot87)$. The Z.P. is that of $F_{22}^2 (\cdot03 - / - - - \cdot94)$. The allocation by S. to $x-p_2(2)$ is that of Randall, but this will not fit in with 36137 as $x-p_1(2)$ for the separation is far too small, and the own law is not obeyed.

The result as to the supposed intercombination lines is collected here. A dot refers to a "forbidden line"; — denotes

that the line has not been observed ; 0 that no Z.P. has been observed.

d^2p^4	s^2p^4	d^2d^4	s^2d^4
— †	•	— †	•
0 *	*	† †	•
* •	§	† †	†
d^2f^4		† •	†
• *	•	d^2p^2	s^2p^2
† —	•	† §	(1) †
* —	•		
$d\ d^2$	s^2d^2	d^4f^2	
† 0	†	† †	
* *§	•		
•	36104†		

It is seen Z.E. is distinctly unfavourable to the allocations which have been based on the supposition that 2042 is a separation due to the difference of two doublet terms.

16. The allocation of lines to $s(2) - M$ etc. by Shenstone must not be passed over without discussion, since if the constitution proposed is sustained, the relation of map IV. to the $S(2)$ linkage must be given up. The lines are given in table i. in the s -column. The separations from the corresponding x -lines are taken to be $x - s(2)$. The value of this can be obtained with extreme accuracy, since $x - s(2) = x - p_1 + p_1 - s(2) = D_{12}' + S_1(2)$, and these two lines have reliable measures. Hasbach agrees with the interferometer measures of F.B. for D_{22}' , and his measure for D_{12}' gives correct ν with this, say correct within $d\lambda = .002$. For $S_1(2)$ we get $8092.74 \pm .02$ by Meggers, $.78$ by both Meissner and Eder, say $.76 \pm .02$. Hence the wave numbers are $17538.238 \pm .006 + 12353.03 \pm .03 = 29891.57 \pm .04$. Or we may arrive at the value through F.B.'s interferometer measure of $y - p_1$ and $\phi = 2042.877$. Thus

$$x - s(2) = 19581.115 + .008 + 12353.33 \pm .03 - 2042.877 \\ = 29891.57 \pm .04.$$

The probable errors of the lines involved are given in (). Those for $s(2) -$ etc. are given by Meggers. In the x column, under those of Hasbach I have inserted what I think are more probable values with probable errors. The separations are

M, 29891.37 (.39)	N, 29890.58 (.29)
K, 91.73 (.5)	R, 92.55 (.47)
J, 90.91 (.40)	

Thus on the hypothesis of an unchanging two-term constitution these values allow real separations for M, K, but exclude J, N, R*.

On the broader basis of links and displacements, however, we can hardly refrain from recognizing the whole set of five pairs as thus related, *i. e.* separated by $x-s(2)$. At the same time, on this basis it will not follow that the small wave numbers refer to combinations of the form $3(2)-t$. This supposition would give for the sets $s(2)-R/D^2$ with D respectively 4.290, 4.743, 5.017, 5.118, 5.275, with no relation to each other. Nothing analogous to this is known amongst other atomic emission lines. Moreover, all these lines lie in the same region as that of S(2), which we already know is distinguished by the number of lines linked and displaced from S(2). Indeed, this is also indicated at a glance by the large number of separations present close to the doublet separation 248.44, from which it may be concluded that the $p(1)$ term or its displacements must be present (see discussion below of 14281). Some of these doublet connexions are shown in table ii.

Again, the presence of $s(2)-t$ lines would point to the existence of much stronger $s(1)-t$, which have not been seen. This objection might perhaps be countered by pointing out that the observed lines by Handke and by L. and E. Bloch in this region are spark produced, and the $s(1)-t$ might be thus obliterated. But McLennan has observed the arc spectrum in this region, and has not seen them. Further doubt must be felt when it is seen that while at least x (M, K, N, R) are definitely related with similar characters, those for the supposed $s(2)-t$ vary in no relation to them. This is clearly seen by the following comparison:—

	M.	K.	J.	N.	R.
x	4	6R	1n	6R	4R
$s(2)$	5	1n	2b	3	3n

Here all the x characters are by Hasbach and the $s(2)$ by Meggers. The relative behaviour of the $s(2)$ are quite out of step with those of the x .

The succession of several equal separations would be easy to explain if the x sets were merely link connected. It would only mean that the successive $s(2)$ lines were linked

* Below λ , 2300 Hasbach reads about $d\lambda = .02$ too small. For (J)—H., Pup., K.R. give a mean 2236.28 and Wolfsohn is .295 *in vacuo*, generally less in air. .28+015 is taken. For (N)—Wolfsohn gives 2227.776 in air and quotes Bidder as .768; K.R. and E.V. both give .77, which must be correct within .01. For (R)—Wolfsohn in air 2215.654 agrees with H. .65—possible error taken = .01.

in the same way as the successive x . But we have seen that this is only the case as between N , R , connected by the a -link. If the dependence of $M \dots$ on $p(2)$ and its displacements is accepted, $p(2)$ must be placed in the same way in the $s(2)-t$, and this is certainly not the case.

The foregoing considerations produce a disposition to accept the exclusion of the J , N , R set, already indicated by the numerical comparison as definite. There remain the M , K to be considered. For the M , 13206 shows no clear relation to other lines, *e.g.* no links or a , b displacements, so that its constitution remains otherwise undetermined. There is no reason therefore, *a priori*, to doubt its constitution as $x M-x+s(2)$, or even as $s(2)-R/(4.290)^2$, except that with its strong intensity of 5 the $s(1)$ representative 56343.7 or $\lambda-1774.8$ (vac.) should have been seen by McLennan.

In the case of K , 14281* is 2 iv, and occurs with its connexions in 5 of table ii.† Here the θ -separations shown deviate so largely from the values that they should probably be excluded, as not real. In this set we have the repetitions of 248.8 and the ϕ -separation. Map IV. gives $14281=S_2(2) \cdot e \cdot n' + .08$ and $14031=(\delta_1) S_1(2) \cdot e \cdot n' - .10$.

Map VIII.

The map as drawn in [I.] was in two parts with several clear pseudo links, and no attempt was made to obtain line formulæ. In the light of the reality of the multiple b displacements, afforded by the preceding discussion, it is possible to re-arrange the map in a more satisfying manner, with the introduction of a few extra lines. The former ordinal numbers are still attached to the old lines, and the new ones run from 16 to 22 and 13 *a*. The map was drawn starting from the $S(3)$ lines, but it includes two satelloids, a clear θ , and the 887 separations. In no other cases are these associated with normal S or D lines, and it would seem necessary to exclude them. If so, the pseudo link must be the first 679.29 with 149. On the other hand, the

* As supporting the validity of map IV. we may take the 14413 and 14201 (in 2. 3 of table ii. and 3, 39 iv). In the discussion in [I.] the formula for 39 was not given, but starting from 2 iv we saw that 132 is due to displacement ($-a$) and 211.6 (3 to 10 iv) to ($-2a+b$) on this. Consequently the -211 of 39 to 3 is ($2a-b$) on 3 iv or ($a-b$) on 2 iv, *i.e.* on p_2 . This shifts -79.77 as against the observed -79.76 .

† In this set 27520, 28200 were not noted in map VI., but they should be added, with its additional 680. 27271 depends on $P_1(-2a-b)$, on which Δ shifts 249.14 (for obs. 249.0.). 28200 may be linked to this by u' .

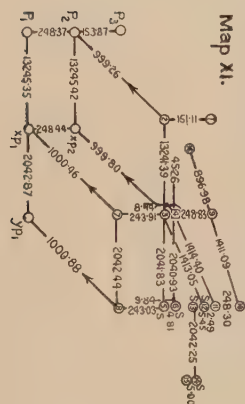
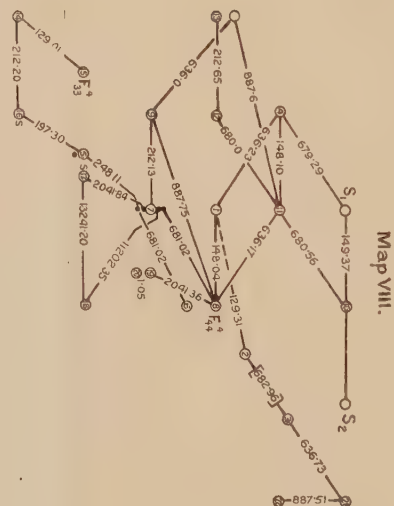
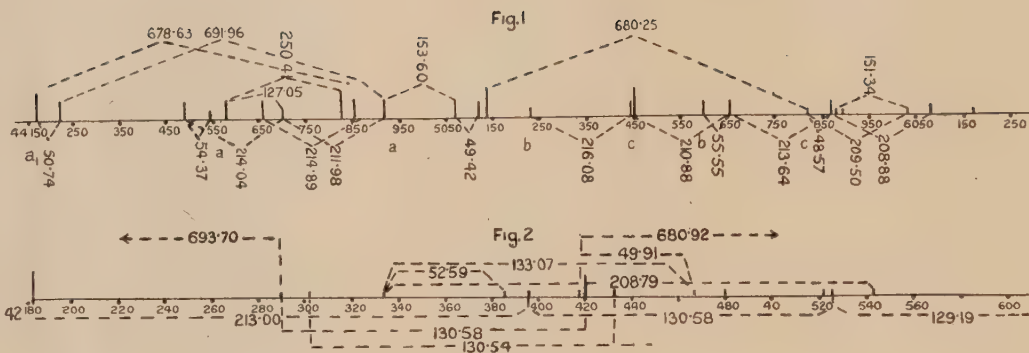
presence of 248, and the a , $2b$, $3b$ displacements require the presence of the $p(1)$ terms. But the relations beyond (8) fit in extremely well, and the formulæ have been worked out on the supposition of a continuous map. This doubt, however, should be kept in mind. The sep. 682.96 is clearly pseudo, and is marked so. The measures of $S_1(3)$, $S_2(3)$ give a separation .09 too large. If the error is in S_1 , .09 should be deducted from all the residuals, and it will be found that the greater number are improved. In any case, the residual in any line is due to the error in S_1 as well as to its own O.E. The own shift in $s(3)$ is .203, and is so small as to allow any rough agreement to be made exact within O.E. by introducing them. Fortunately, however, the s -term is much less subject to displacement than the p , and agreement has been reached without introducing multiple displacements except in 10, 11, 12, 13, where a common 3δ (shift .61) seems called for. It would be met numerically by y , but this part of the map appears to belong to $S(3)$, where the satelloids do not occur. This general agreement, arrived at without displacements on the current term, does not necessitate the supposition that the map belongs to $S(3)$. The p_1 term must enter, and the map may start from a line $=p_1(1) + \text{links} - \text{some other term}$. The Zeeman effect seems to indicate that this term is an f .

$$S_1(3) = 22064.78 ; S_2(3) = 22313.31.$$

The S denotes $S_1(3)$.

- 10, 22214.18, 149.39 ahead of S_1 ,
 $-3b$ on p_1 shifts 148.74 $= (-3b)S(3\delta_1) + .04$
 4, 21385.50, is $u - 1.34$ from S_1 $= u.(-\delta_1)S + .10$
 11, 21533.6, 148.10 ahead $= u.(-3b)S(3\delta_1) + .09$
 E.H. give ... 32.25 or a collateral δ_1 on p_1 .
 12, 20853.6, $u' - .06$ behind $= u.u'(-3b)S(3\delta_1) + .13$
 13, 20640.95, 212.65 behind $= u.u'.Y_2.(-3b)S(3\delta_1) + .04$
 13a, $2n$, 4842.2; 20646.0—see p. 1209.
 1, 22021.73, 636.23 on (4) $= u.S.3Y_2 + .05$
 8, 22169.77, 148.13 on (1) $= u.(-3b)S.3X_2 + .06$
 2, 22151.04, 129.31 on (1), $-a$ on p_1
 shifts 128.84 $= u'.(-a)S.3Y_2 - .13$
 K.R. and E.H. agree with ... 50.89 $u.(-a)S.X_2.2Y_2 + .01$
 7, 21494.15, red sat. ... 88.75 or if exact $9y = .27$ larger
 corrected red satellite $= 2u.(-3b)S.3X_2 + .06$
 main line $= 2u(-3b)S.3X_2 + 9y - .06$
 viol. sat. $= 7y - .16$ $= 2u(-3b)S.3X_2 + 16y - .22$
 6, 22179.0 $= u(-3b)S.3X_2 + 16y + .17$
 9, 21282.02, 212.13 behind (7) $= 2u.(-3b)S.2X_2 - 9y - .08$
 5, 21249.876, 248.10 behind viol. of (7)

The 248 suggests a $5b$ displacement or the doublet v as a



link; $5b$ on $(-3b)$ shifts only 247·28. The two suppositions require respectively

$$2u \cdot (2b)S \cdot 3X_2 + 14y + \cdot 10$$

and $v \cdot 2u \cdot (-3b)S \cdot 3X_2 + 16y + \cdot 12,$

the first requiring the introduction of $2y$. The succeeding lines support the second allocation.

16, $2s$, 4748·85 E.V.; 21052·57 is 197·30 behind. $(4b)$ on $(2b)$ to $(6b)$ S shifts 195·75; on $(-3b)$ it shifts 198·05, and fits better the second allocation of (5). It gives $v \cdot 2u \cdot (b)S \cdot 3Y_2 - 16y + \cdot 06$

14, 20840·37, 212·20 behind $v \cdot u \cdot u'(b)S \cdot Y_2 \cdot X_2 + 16y + \cdot 10$

15, 20969·38, 129·01 ahead, $-a$ on $(b)p$ shifts 129·15
 $= v \cdot 2u'(-a+b)S \cdot Y_2 \cdot X_2 + 16y - \cdot 03$
 $-a$ on $(6b)p$ shifts 127·08, again supports the second.

17, $2ns$, 5139·03, E.V.; 19454·16, 2041·84 $= 3u + \cdot 05$ is a pure $3u$ link to a spark line $= 5u(-3b)S \cdot 3X_2 + 12y + \cdot 07$

18, 1, 3057·65; 32695·36. The linked $3u$ line (17) is not ϕ . The line is separated from a $2y$ red sat. of (7) by 11202·35 or $s(1) - y - \cdot 1$, which justifies its inclusion as a θ line $= (17) - 2y + \theta$

19, 1, 4966·72, E.H.; 20128·41. } The second is 2040·25 behind 8
 $= u \cdot 3u'(-3b)S \cdot 3X_2 - \cdot 01$

20, 1, ... 66·46, E.H.; ... 29·46. } The first is then $2y - \cdot 09$ less
 $= 3u \cdot u'(-3b)S \cdot 3X_2 + \cdot 08$

3, 22834·0. The 682 is probably not u . If real, formula
 $= (-a)S \cdot 3X_2 + 3 \cdot 68$

21, $2n_{br}$, 4259·43; 23470·73 $= (-a)S \cdot 6X_2 + 3 \cdot 60$

22, 2, 4104·223; 24358·24 $= \dots + u' + X_1 - 4y$

Map XI.

(For lines, see No. 8 of table ii.)

Map XII.

1. 3, 3279·823	30480·697 S 6 i	22. $1n$, 2138·44	46748·26 H; 7·17 ⁽¹⁾
2. 4, 3208·236	31160·804 S 5 i	23. 3, 1725·9	57942·7 Hke.
3. $1n$, 3209·47	31148·83 S 5 ii	24. 2194·41	45556·06 P.
4. 6, 3194·103	31298·677 S 17 ii	25. $1n$, 3171·658	31520·163
5. 4, 3073·803	32523·569 S iii	26. $1n$, 3151·61	31720·66 22 ii
6. 5, 3010·840	33203·677 S 7 iii	27. 3, 3156·625	31670·284 23 ii
7. 4, 2997·363	33352·963 $13a$ iii	28. 6, 3126·106	31979·438 18 ii
8. 2, 2998·384	33341·608 13 iii	29. $2n$, 2979·38	33554·22 12 iii
9. 8, 2824·373	35395·672	30. 6, 2961·177	33760·521 S 10 iii
10. $3n$, 3175·73	31479·757 i	31. $2n$, 2978·293	33566·508 12a iii
11. $6n$, 3108·603	32159·491 S 8 i	32. $1n$, 2991·76	33415·42 17 iii
12. 1, 2982·16	33522·99 E.H.	33. 6, 3093·993	32311·342 S 4 iii
13. 1, 2922·87	34202·96 E.H.	34. 3, 3088·121	32372·781 25 ii
14. $2n$, 3014·84	33159·649 i	35. 4, 3128·692	31953·008 26 ii
15. $1n$, 3392·01	29472·61 11 i	36. 2, 3149·501	31741·899 27 ii
16. 2, 3331·09	29481·56 K.R. $11a$ i	37. $2n$, 3030·25	32991·00 6 iii
17. 3, 3472·136	28792·500 12 i	38. 1, 3361·96	29736·05 46 vi
18. 2, 2244·240	44544·659	39. 2, 3068·912	32575·399 16 iii
19. 4, 2246·984	44490·275	40. $2n$, 3012·02	33190·68
20. $1n$, 2236·22	44704·40	41. $2n$, 3465·40	22848·45 44 vi
21. $2R$, 2225·665	44916·378	42. 1, 2791·95	35806·73

(¹) Dreblow.

The measured sateloids of Hasbach are represented by dots vertically aligned with the main line. Additional sateloids by Stücklen (not measured) are denoted by dots south-west of the main line.

The two ϕ , forward and back from (30), should be noted. They form an undoubted succession of equal ϕ separations from the satellite. K.R.'s reading for (42) is 35806.32 and gives 2042.84.

For general discussion, see §9:—39 is 1413.46 from the 1st satellite ($2y$) of 2 or 1412.89 from an unobserved $3y$. Stücklen gives $3r$, $5v$. The chain 40 to 41 should be noted with the ϕ sep: = $3u$ link. The map is noted for the number of satelloids involved and the number of links made exact within O.E. by suitable choice of satellite. 35 is 14 xiii, which introduces another parallel set to 10, 11, 13, and gives a chain connecting p_f and B.

Map XIII.

- | | |
|-------------------------------------|----------------------------------|
| (1) 2, 1774.4, 56358.9. | (16) 1, 2483.27, 40257.33 |
| (2) 2, 1713.0, 58379.0. | (Hup.). |
| (3) 4, 1693.4, 59052.8 (McL.). | (17) $1n$, 2363.20, 42302.54. |
| (4) 6, 1686.99, 59277.17. | (18) 2, 3700.532, 27015.482. |
| (5) 1, 1703.7, 58697.7. | (19) 3, 3440.52, 29057.08. |
| (6) 2, 2210.240, 45229.807. | (20) 2, 3517.029, 28424.990. |
| (7) $6R?$, 2199.57, .73, 45449.19, | (21) 2, 3671.969, 27225.621. |
| 5.89. | (22) 2, 4003.038, 24973.993. |
| (8) 3, 2189.599, 45656.77. | (23) $1n$, 4242.26, 23565.73. |
| (9) $3n$, 2179.37, 45870.41. | (24) $1n$, 2701.01, 37012.22. |
| (10) $2n$, 2169.49, 46079.29. | (24a) 2, 2630.002, 38011.47. |
| (11) $1n$, 2356.80, 42417.42. | (25) $1n$, 2911.21, 34339.95. |
| (12) $1n$, 2171.75, 46031.34. | (26) $1n$, 3171.658, 31520.163. |
| (13) $4n$, 2079.47, 48073.79 (de | (27) $2n$, 2979.38, 33554.22. |
| Rubies). | (28) $2n$, 2978.293, 33566.508. |
| (14) 4, 3128.692, 31953.008. | (29) 4, 1989.24, 50255.55. |
| (15) 1, 1730.5, 57788.70. | |

The n of the ultra-violet lines 1 ... 5 and 15 are subject to uncertainties about $-35d\lambda$, with $d\lambda$ considerable except in (4), where it is probably $< .05$. In the θ -separations, the 132 ... is represented by a —, thus 13260 is entered —60 etc. A comparison of Handke's with Bloch's measures of apparently the same line seem to show that the former's are from .3 to .5 Å too small. In other words, his wave numbers may be subject to a correction of the order $+10$ to $+16$.

The map contains four different chains. To prevent confusion, they are distinguished by thick, thin, and dotted connexion lines.

27, 28 possibly correspond to a u , v interchange—in which case the separations shown to yp_g have no reference to 1412. 26. xp_g is a satelloid for which Stücklen gives $8r$, $6v$.

Hasbach gives $4y$ and $5y$; one at $10y$ would make the sep. = 1412.72.

The four separations 6-10 form a series inequality = $2(X_2 + Y_2) - .14$ or replacing the 208.86 by the 209.50,

$$= 4Y_2 - .02,$$

pointing thus to link reality. So also

$$xM, yM, sp_s = \phi + u + 0.$$

14 is 35 xii—26 is 25 xii—27 is 29 xii.

Errata in [I].

P. 198. Sat. (12), the W.N. of the satellite should be corrected from .55 to .28. This necessitates the following alterations:—

Sat. (12). 1.79 for 2.06 ; $3y = 1.71$ for $4x =$; y for x .

P. 223. No. 8, .28 for .55; $3y - .05$ for $4x - .10$.

Map I. 5-8-10 read 999.35, 680.35.

Map II. 5 i-8 i-26 read 999.35, 208.27.

Map III. 8 i-10 i read 680.35.

P. 218, l. 12, read $-4a + b$ for $-4a$.

P. 230, l. 10, read .30 for .73.

P. 232. The formulæ were wrongly calculated on D_1 instead of D_2 .
Read respectively (a) $D_2 + .47$; e. (a) $D_2 + .46$; Y_2 . (a) $D_2 + .38$
and add, in place of footnote 7, residuals due to $d\lambda = .06$ in $D_2(4)$,
measured to .1.

Map IV. Between (40) (42), read 49.76 for 44.76.

Map VI. „ (6) (10) (9), read 210.53, 681.81.

„ „ (32) (31) (35), draw the 690.90 between (32) (35)
instead of (31) (35) and delete 133.07 (33).

Map VII. For links to (37) read 48.02, 678.02.

Map IX. Between (1) (4) append arrow pointing up.

Also Map VI. Between (5) (2) read 680.11.

See note to (1), table iv. of this paper.

Add. The addition referred to in note 2, p. 1223.

CIII. *On the Scattering of Radiation from Atoms.*

By IVAR WALLER*.

THE Kramers-Heisenberg dispersion formula gives the radiation scattered from an atom for wave-lengths long compared with atomic dimensions. This formula has been deduced from the principles of wave-mechanics by Schrödinger† and Klein‡. Following a procedure analogous to that of Klein, we deduce in § 1 of the following paper a dispersion formula, which also gives the radiation scattered from an atom for wave-lengths short compared with atomic dimensions. In § 2 we use this formula to find the gradual transformation of the scattering process as the wave-length varies. For long waves we have the dispersion given by the Kramers-Heisenberg formula, and, for sufficiently short waves, a pure Compton effect. In § 1 the approximation to the eigenfunctions of the continuous spectrum given by plane de Broglie waves is discussed, and also the expansion of the wave-functions of the stationary states in Fourier integrals. The corrections due to the spin of the electrons are neglected in this paper §.

§ 1. A wave-function u , corresponding to the motion of an electron in an electromagnetic field of vector potential \mathbf{A} and scalar potential V , must satisfy one of the equations ||

$$-\frac{\hbar^2}{4\pi^2} \left(\nabla^2 u - \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2} \right) \pm 2 \frac{\hbar}{2\pi i} \frac{e}{c} \left(\mathbf{A} \nabla u + \frac{V}{c} \frac{\partial u}{\partial t} \right) + \left[\mu^2 c^2 + \frac{e^2}{c^2} (\mathbf{A}^2 - V^2) \right] u = 0, \quad (1)$$

where $-e$ is the charge and μ the mass of the electron. We consider an atomic field defined by $V = V_0$, $\mathbf{A} = 0$.

Putting

$$u = \phi e^{\frac{2\pi i \mathbf{E} t}{\hbar}} \quad \text{and} \quad \mathbf{E} = \mathbf{E}' + \mu c^2,$$

* Communicated by Prof. W. L. Bragg, F.R.S.

† E. Schrödinger, *Ann. d. Phys.* lxxxi. p. 108 (1926).

‡ O. Klein, *Zeits. f. Phys.* xli. p. 407 (1927).

§ A summary of the results arrived at in this paper has been given in a letter to 'Nature,' July 30, 1927, unfortunately without knowledge of a paper by G. Wentzel, *Zeits. f. Phys.* xliii. p. 1 (1927), who has used a dispersion formula for short waves to investigate the Compton effect of bound electrons. Some of the results given in that letter have already been obtained by Wentzel.

|| Cf. e. g., Klein, *loc. cit.*

we find on substitution in (1), taking the negative sign for the second term,

$$\nabla^2 \phi + \frac{8\pi^2 \mu}{h^2} (E' + \epsilon V_0) \phi + \frac{4\pi^2}{h^2 c^2} (E' + \epsilon V_0)^2 \phi = 0. \quad (2)$$

Let ϕ_n be a normalized eigenfunction ("Eigenfunktion") satisfying this equation, which is continuous and finite throughout space, and let the corresponding characteristic value ("Eigenwert") of E' be E_n' . We put

$$u_n = \phi_n e^{\frac{2\pi i E_n t}{h}} \quad \text{and} \quad E_n = E_n' + \mu c^2.$$

Corresponding to an atomic problem, we assume that all positive values of E' form a continuous set of characteristic values. For $E' < 0$ an infinite set of discrete characteristic values may be found. For the calculations made here it is formally important to have only discrete and not degenerated eigenfunctions. We may attain this by assuming the presence of distant boundary walls to which corresponds the boundary conditions $\phi = 0$.

The last term on the left side of (2) gives a relativity correction. Neglecting this term, we get the well-known equation

$$\nabla^2 \phi + \frac{8\pi^2 \mu}{h^2} (E' + \epsilon V_0) \phi = 0. \quad \dots \quad (2')$$

A light-wave falling on the atom can be defined by

$$V = 0, \quad A = -\sigma \frac{c}{4\pi i \nu} \left[E_0 e^{2\pi i \nu \left(t - \frac{nr}{c}\right)} - \tilde{E}_0 e^{-2\pi i \nu \left(t - \frac{nr}{c}\right)} \right]. \quad (3)$$

The vector r may be drawn from the nucleus as origin. The sign \sim denotes the conjugate value. σ is a perturbation parameter. The electric field of the light-wave is

given by the real part of $E_0 e^{\frac{2\pi i \nu \left(t - \frac{nr}{c}\right)}{h}}$. As a first approximation, the perturbed wave-functions may be written in the form $u_n + \sigma f_n$. In the equation for f_n , obtained in the usual way, we neglect the term containing $(E_n' \pm h\nu + \epsilon V_0)^2$, which gives a relativity correction. From a calculation which is analogous to the corresponding calculation for long waves given by Schrödinger, we find

$$f_n = -\frac{\epsilon}{8\pi^2 \mu \nu} \left[e^{\frac{2\pi i}{h} (E_n + h\nu)t} \sum_s \frac{E_0 A_{ns}}{\nu_{ns} + \nu} \phi_s + e^{\frac{2\pi i}{h} (E_n - h\nu)t} \sum_s \frac{\tilde{E}_0 \tilde{A}_{sn}}{\nu_{ns} - \nu} \phi_s \right], \quad \dots \quad (4)$$

putting

$$A_{ns} = \int \tilde{\phi}_s e^{-\frac{2\pi i \nu}{c} nr} \nabla \phi_n dv, \quad \nu_{ns} = \frac{E_n - E_s}{h}. \quad \dots \quad (4')$$

We now use the well-known formulæ of wave mechanics for charge-density and current-density* in a way closely analogous to that given by Klein†. Putting $\sigma=1$, we then find the following values of the charge-density ρ_n and the current-density \mathbf{I}_n , which determine the radiation scattered from an atom in the initial state n :

$$\left. \begin{aligned} \rho_n &= \sum_m^{\mathbf{E}_m < \mathbf{E}_n + \hbar\nu} (\rho_{nm} + \tilde{\rho}_{nm}) + \sum_m^{\mathbf{E}_m < \mathbf{E}_n - \hbar\nu} (\rho_{mn} + \tilde{\rho}_{mn}) \\ \mathbf{I}_n &= \sum_m^{\mathbf{E}_m < \mathbf{E}_n + \hbar\nu} (\mathbf{I}_{nm} + \tilde{\mathbf{I}}_{nm}) + \sum_m^{\mathbf{E}_m < \mathbf{E}_n - \hbar\nu} (\mathbf{I}_{mn} + \tilde{\mathbf{I}}_{mn}) \end{aligned} \right\}, \quad (5)$$

putting

$$\left. \begin{aligned} \rho_{nm} &= \frac{\epsilon^2}{8\pi^2\mu\nu_s} \sum_s (B_{ns}\tilde{\phi}_m\phi_s - B_{sm}\phi_n\tilde{\phi}_s) e^{2\pi i(\nu_{nm}+\nu)t} \\ \mathbf{I}_{nm} &= -\frac{i\epsilon^2}{4\pi^2\mu\nu} \left[\mathbf{E}_0\phi_n\tilde{\phi}_m e^{-\frac{2\pi i\nu}{c}\mathbf{r}\mathbf{n}} - \frac{h}{8\pi^2\mu_s} \sum_s (B_{ns}\mathbf{C}_{ms} \right. \\ &\quad \left. - B_{sm}\mathbf{C}_{sn}) \right] e^{2\pi i(\nu_{nm}+\nu)t} \end{aligned} \right\} \quad (5')$$

$$B_{ns} = \frac{\mathbf{E}_0\mathbf{A}_{ns}}{\nu_{ns} + \nu}, \quad \mathbf{C}_{ns} = \tilde{\phi}_n \nabla \phi_s - \phi_s \nabla \tilde{\phi}_n. \quad (6)$$

It is easily confirmed that $\text{div } \mathbf{I}_{nm} + 2\pi i(\nu_{nm} + \nu)\rho_{nm} = 0$, and that the normalization conditions are fulfilled. From well-known formulæ of the Maxwell theory‡, one finds that the radiation scattered from the atom in a direction given by \mathbf{n}' , and corresponding to \mathbf{I}_{nm} (and ρ_{nm}) may, for great distances from the atom, be deduced from the dipol moment

$$\begin{aligned} \mathbf{d}_{nm} &= -\frac{1}{4\pi^2\nu(\nu_{nm} + \nu)} \frac{\epsilon^2}{2\mu} \left[\mathbf{E}_0\delta_{nm} \right. \\ &\quad \left. + \frac{h}{4\pi^2\mu_s} \sum_s (B_{ns}\tilde{\mathbf{A}}_{ms}' - B_{sm}\tilde{\mathbf{A}}_{sn}') \right] e^{2\pi i(\nu_{nm}+\nu)t}, \quad (7) \end{aligned}$$

putting

$$\mathbf{A}_{ns}' = \int \tilde{\phi}_s e^{-\frac{2\pi i}{c}(\nu_{nm}+\nu)\mathbf{n}'\mathbf{r}} \nabla \phi_n dv, \quad (7')$$

$$\delta_{nm} = \int \phi_n \tilde{\phi}_m e^{\frac{2\pi i}{c}[(\nu_{nm}+\nu)\mathbf{n}' - \nu\mathbf{n}]\mathbf{r}} dv. \quad (7'')$$

* Cf. W. Gordon, *Zeits. f. Phys.* xli. p. 117 (1926).

† Klein, *loc. cit.*

‡ The formulæ (38), (40) and (41) in the paper by Klein, *loc. cit.* give

$$\mathbf{d}_{nm} = \int \mathbf{I}_{nm} e^{2\pi i(\nu_{nm}+\nu)\mathbf{n}'\cdot\mathbf{r}/c} dv / 2\pi i(\nu_{nm} + \nu).$$

The total radiation scattered from an atom in the initial state n may accordingly be derived from the following sum of dipol moments :

$$E_m < E_n + h\nu \quad \dots \quad E_m < E_n - h\nu$$

$$\sum_m (\mathbf{d}_{nm} + \tilde{\mathbf{d}}_{nm}) + \sum_m (\mathbf{d}_{mn} + \tilde{\mathbf{d}}_{mn}). \quad (8)$$

According to (6) it may be expected that, for large values of ν , only the term $\mathbf{E}_0 \delta_{nm}$ in the bracket [] of (7) is of importance. We shall investigate this point in § 2. The corresponding part of \mathbf{d}_{nm} comes from that part of the wave mechanical current-density which is formed by the product of the vector potential of the light-wave and the unperturbed wave-functions.

Assuming the unperturbed wave-functions to be real, one finds that the dipol moment \mathbf{d}_{nn} is given by

$$\mathbf{d}_{nn} = -\frac{1}{4\pi^2\nu^2} \frac{\epsilon^2}{2\mu} \left[\mathbf{E}_0 \delta_{nn} + \frac{h}{4\pi^2\mu} \sum_s \frac{\nu_{ns} (\mathbf{E}_0 \mathbf{A}_{ns}) \tilde{\mathbf{A}}_{ns}'}{\nu_{ns}^2 - \nu^2} \right] e^{2\pi i \nu t}. \quad (9)$$

For wave-lengths long compared with atomic dimensions, we must get the Kramers-Heisenberg dispersion formula*. In this limit all exponentials, except those containing the time, are to be put equal to unity. If

$$\mathbf{D}_{ns} = -\epsilon \int \mathbf{r} \phi_n \tilde{\phi}_s dv,$$

it then follows

$$\mathbf{A}_{ns} = \mathbf{A}_{ns}' = -\frac{4\pi^2\mu}{h\epsilon} \nu_{ns} \mathbf{D}_{ns}.$$

The relations †

$$\frac{\nu_{ms}}{\nu_{ns} + \nu} = 1 - \frac{\nu_{nm} + \nu}{\nu_{ns} + \nu}, \quad \frac{\nu_{ns}}{\nu_{ms} - \nu} = 1 + \frac{\nu_{nm} + \nu}{\nu_{ms} - \nu}. \quad (9')$$

$$\left. \begin{aligned} \sum_s [\nu_{ns} (\mathbf{E}_0 \mathbf{D}_{ns}) \mathbf{D}_{sm} + \nu_{ms} (\mathbf{E}_0 \mathbf{D}_{sm}) \mathbf{D}_{ns}] &= -\mathbf{E}_0 \frac{\epsilon^2 h}{4\pi^2 \mu} \delta_{nm} \\ \sum_s [(\mathbf{E}_0 \mathbf{D}_{ns}) \mathbf{D}_{sm} - (\mathbf{E}_0 \mathbf{D}_{sm}) \mathbf{D}_{ns}] &= 0, \end{aligned} \right\} \quad (9'')$$

then give

$$\mathbf{d}_{nm} = -\frac{1}{2h} \sum_s \left[\frac{(\mathbf{E}_0 \mathbf{D}_{ns}) \mathbf{D}_{sm}}{\nu_{ns} + \nu} + \frac{(\mathbf{E}_0 \mathbf{D}_{sm}) \mathbf{D}_{ns}}{\nu_{ms} - \nu} \right] e^{2\pi i (\nu_{nm} + \nu) t}.$$

In order to find a simple approximation to the wave-functions of the continuous spectrum we may assume \mathbf{E}' to

* About the existence of the incoherent radiation, cf. A. Smekal, *Naturw.* xi. p. 873 (1923).

† The relations (9'') follow directly from Heisenberg's matrix theory and are also easily obtained from (2').

be large compared with ϵV_0 . Neglecting ϵV_0 in (2), we get the wave equation for a free electron which has the solution

$$\phi_s = C_s e^{-\frac{2\pi i}{h} \mathbf{M}_s \mathbf{r}} \quad . \quad . \quad . \quad (10)$$

for $E = E_s$, if

$$\mathbf{M}_s^2 - \frac{1}{c^2} E_s^2 + \mu^2 c^2 = 0, \quad C_s = \frac{1}{\sqrt{v}} \sqrt{\frac{\mu c^2}{E}}; \quad . \quad (10')$$

v is the volume inside the boundary walls. The value of C_s follows from the relativistic normalization condition. The wave-function corresponding to ϕ_s represents the de Broglie wave of a free electron, having the energy E_s and the momentum \mathbf{M}_s . To each element h^3 of phase space must correspond one state of the electron. The number of eigenfunctions ϕ_s belonging to the element $d\tau = d\mathbf{M}_x d\mathbf{M}_y d\mathbf{M}_z$ of the momentum space is therefore $v h^{-3} d\tau$. Neglecting relativity corrections, we find instead of (10'),

$$E_s' = \mathbf{M}_s^2 / 2\mu, \quad C_s = \frac{1}{\sqrt{v}}. \quad . \quad . \quad (10'')$$

It is often useful to regard the wave-functions of any state n as a group of plane de Broglie waves. We may for that purpose put ϕ_n into the form of a Fourier integral

$$\phi_n = \int C_{\mathbf{M}}^{(n)} e^{-\frac{2\pi i}{h} \mathbf{M} \mathbf{r}} d\tau. \quad . \quad . \quad . \quad (11)$$

If n is a state for which relativity corrections in the normalization condition can be neglected, it then follows

$$\int |C_{\mathbf{M}}^{(n)}|^2 d\tau = h^{-3}. \quad . \quad . \quad . \quad (11')$$

A mean value M_n^2 of the square of the momentum for the state n may be defined by the formula

$$M_n^2 = \overline{\mathbf{M}^2} = h^3 \int |C_{\mathbf{M}}^{(n)}|^2 \mathbf{M}^2 d\tau. \quad . \quad . \quad . \quad (12)$$

We then find from (2')

$$M_n^2 = 2\mu(E_n' + \overline{\epsilon V_0}) = 2\mu \overline{E_{\text{kin}}^{(n)}}. \quad . \quad . \quad . \quad (12')$$

Here $-\overline{\epsilon V_0}$ is the mean value (defined according to Schrödinger) of the potential energy in the state n . $\overline{E_{\text{kin}}^{(n)}}$ may therefore be regarded as the corresponding mean value of the kinetic energy.

For a Coulomb field ($V_0 = \frac{N\epsilon}{r}$) we have the relation of Bohr,

$$\overline{E_{\text{kin}}^{(n)}} = -\frac{1}{2} \overline{E_{\text{pot}}^{(n)}} = -E_n' = \frac{N^2 \epsilon^2}{2n^2 a_H}, \quad \left(a_H = \frac{h^2}{4\pi^2 \mu \epsilon^2} \right). \quad (13)$$

Therefore $M_n = \frac{Nh}{2\pi n a_H}$. For the normal state ($n=1$) we find

$$C_{\mathbf{M}}^{(1)} = \frac{2\sqrt{2}}{\pi} \frac{h^{-3} M_1^5}{(M_1^2 + M^2)^2} \cdot \cdot \cdot \cdot \cdot \quad (13')$$

For a Coulomb field, it also follows that $C_{\mathbf{M}}^{(n)}$ decreases at least as rapidly as M^{-4} if $|\mathbf{M}|$ tends to infinity. For any atomic field here considered, we may assume $C_{\mathbf{M}}^{(n)}$ to decrease so rapidly for increasing $|\mathbf{M}|$ that $C_{\mathbf{M}}^{(n)}$ is small, if $|\mathbf{M}|$ is much bigger than M_n . n then denotes a low state.

Taking relativity corrections into account, we can find a dispersion formula for very short waves in the following way:—Assuming $h\nu$ to be much bigger than $-E_1'$, we can neglect ϵV_0 in the equation giving f_n (cf. p. 1229). This equation may then be solved by expansions referring to the orthogonal functions (10). In this way* we find a dispersion formula which is similar to (7). Now, however, the quantities

$$[(E_n + h\nu)^2 - E_s^2]/2hE_s \quad \text{and} \quad [(E_m - h\nu)^2 - E_s^2]/2hE_s$$

have taken the place of the denominators $\nu_{ns} + \nu$ and $\nu_{ms} - \nu$. In the relations (4') and (7') ϕ_s is now a function (10). ϕ_n and ϕ_m are generally solutions of (2).

§ 2. We shall now enter upon a discussion of the distribution of intensities amongst the various frequencies of the scattered radiation. The initial state n is assumed to be a low state of the atom, for which relativity corrections may be neglected.

We shall investigate first the *coherent* radiation which is deduced from the dipol moment \mathbf{d}_{nn} . The wave-length λ of the incident radiation is first assumed to be large compared with D_n , a measure of the linear dimensions of the atom in the initial state n . \mathbf{d}_{nn} is then given by the Kramers-Heisenberg formula. The first term in the bracket [] of (7) is equal to \mathbf{E}_0 . If, having due regard to the limits of λ , $h\nu$ can be chosen much bigger than the ionization energy

* In this case the normalization conditions are only approximately fulfilled.

$-E_1'$ of the normal state, the second term in that bracket will be small and can be neglected. It is easily found that the intensity of the scattered coherent radiation is then given by the classical formula of J. J. Thomson.

We then assume ν to be so big that λ is comparable with or less than D_n . δ_{nn} must now be less than unity, since the exponential factor in (7'') takes both positive and negative values in those parts of space from which some contribution to this integral is obtained. Using (11), we find

$$\delta_{nn} = h^3 \int C_{\mathbf{M}}^{(n)} C_{\mathbf{M}+\mathbf{M}_R}^{(n)} d\tau. \quad . \quad . \quad . \quad (14)$$

Here $\mathbf{M}_R = \frac{h\nu}{c}(\mathbf{n} - \mathbf{n}')$ is the momentum imparted to the electron at the scattering of one light quantum. Now, according to a previous assumption, $C_{\mathbf{M}}^{(n)}$ is small if $|\mathbf{M}|$ is much greater than M_n . According to (14), δ_{nn} must therefore be small if $|\mathbf{M}_R| \gg M_n$. The second term in the bracket of (7) is to be neglected as before, if $h\nu \gg -E_1'$. For sufficiently high frequencies the coherent radiation therefore disappears*.

Since generally for $h\nu \gg -E_1$ only the first term $E_0\delta_{nn}$ in the bracket [] of (7) is to be taken into account, it also follows that the scattered radiation can in this case be directly calculated from the Schrödinger density of charge $\rho_n^{(0)} = -e|\phi_n|^2$, assuming each volume element dv to scatter classically as a free particle with the mass $-\mu\rho_n^{(0)}dv/e$ and the charge $\rho_n^{(0)}dv$.

The *incoherent* scattered radiation is given by those terms in the sum (8) for which $m \neq n$. The wave-length of the incident radiation is at first assumed to be large compared with D_n , so that $\delta_{nm} = 0$. If $h\nu$ is of the same order of magnitude as $-E_1'$ the second term in the bracket [] of (7) may sometimes be large enough to give a measurable incoherent radiation. If, taking the limits of λ into account, $h\nu$ can be chosen much bigger than $-E_1'$, this second term will generally be so small that the corresponding radiation—the intensity of which is proportional to the square of this term—can be neglected. For $h\nu > E_n - E_1$ only the first sum in (8) is to be taken into account.

If the frequency ν becomes so large that λ is comparable with, or less than D_n , the term $E_0\delta_{nm}$ must be taken into account. An incoherent radiation of various frequencies is

* Except, of course, in the direction of the incident wave.

then obtained. For states m belonging to the continuous term spectrum of the atom, the corresponding scattering frequencies $\nu_{nm} + \nu$ form a continuous spectrum. The scattering of a quantum of each of these frequencies is of course connected with the ejection of the electron from the atom. Assuming \mathbf{n} and \mathbf{n}' to be fixed, the distribution of intensity amongst these frequencies must, for sufficiently high frequency ν , show a hump which, as ν increases, goes over into the sharp peak corresponding to the pure Compton effect. We shall investigate this point, assuming that the approximation (10) may be used for the wave-functions ϕ_m , taking $s = m$. This implies the condition $E_m' \gg -E_n'$. It is easily seen that we may find the value of the second term in the bracket of (7) with fair accuracy by using the approximation (10) for ϕ_s . Taking for ϕ_n the expression (11), the sums and integrals occurring in the formula can be evaluated. The expression for d_{nm} thus found differs from that following from the relativistic formula mentioned at the end of § 1 only by relativity corrections. The last-mentioned expression must give a better approximation for high frequencies ν . This expression is * :

$$d_{nm} = - \frac{1}{4\pi^2\nu\nu'} \frac{\epsilon^2}{2\mu} \sqrt{\frac{\mu c^2}{E'}} \frac{h^3}{\sqrt{\nu}} C_{\mathbf{M}' + \kappa'\mathbf{n}' - \kappa\mathbf{n}}^{(n)} \left\{ E_0 + \right. \\ \left. + 2c^2 \left[\frac{[E_0(\mathbf{M}' + \kappa'\mathbf{n}')] \mathbf{M}'}{(E_n + h\nu)^2 - E_{\mathbf{M}' + \kappa'\mathbf{n}}^2} + \frac{(E_0\mathbf{M}')(\mathbf{M}' - \kappa\mathbf{n})}{(E' - h\nu)^2 - E_{\mathbf{M}' - \kappa\mathbf{n}}^2} \right] \right\} e^{2\pi i\nu' t}. \quad (15)$$

Here $E' = E_m$, $\mathbf{M}' = \mathbf{M}_m$, $\nu' = \nu_{nm} + \nu = (E_n - E')/h + \nu$, $\kappa = h\nu/c$, and $\kappa' = h\nu'/c$. According to (10') we have the relation $\mathbf{M}'^2 - E'^2/c^2 + \mu^2 c^2 = 0$. Assuming ν , \mathbf{n} , and \mathbf{n}' to be fixed, these relations may be used to express ν' in terms of \mathbf{M}' . Since $E_m \gg -E_n$ and $E_m = E'$, we have approximately

$$h\nu = h\nu' + E'. \quad (16)$$

Let us now take a value of \mathbf{M}' , \mathbf{M}_c' say, satisfying the relation

$$\mathbf{M}' + \kappa'\mathbf{n}' - \kappa\mathbf{n} = 0. \quad (16')$$

We denote the corresponding value of ν' by ν_c . (16) and (16') are the relations expressing the conservation of energy and momentum for the Compton effect of a free electron. In this case \mathbf{M}_c is the momentum imparted to the electron

* This formula is not valid if any of the denominators vanish.

and ν_c the frequency of the scattered radiation. Putting the corresponding frequency displacement $\nu - \nu_c = \Delta\nu_c$, we find, assuming $\mathbf{M}' - \mathbf{M}_c$ to be small compared with \mathbf{M}_c ,

$$\frac{\nu' - \nu_c}{\Delta\nu_c} = - \frac{(\mathbf{M}' - \mathbf{M}_c) \cdot \mathbf{M}_c}{\mathbf{M}_c^2 + \mu^2 c^2} \cdot \cdot \cdot \cdot (17)$$

If $h\nu < \mu c^2$, \mathbf{M}_c is of course, to a first approximation, equal to $h\nu(\mathbf{n} - \mathbf{n}')/c$. If the direction of \mathbf{n}' is not the same as that of \mathbf{n} , it is always possible to satisfy the condition $|\mathbf{M}_c| \gg M_n$ by choosing ν big enough. According to (17), to values of $\nu' - \nu_c$ which are not small compared with $\Delta\nu_c$, correspond values of $|\mathbf{M}' - \mathbf{M}_c| = |\mathbf{M}' + \kappa'\mathbf{n}' - \kappa\mathbf{n}|$ large compared with M_n . According to previous assumptions, $C_{\mathbf{M}' + \kappa'\mathbf{n}' - \kappa\mathbf{n}}^{(n)}$ is then small. For values of $M_n/|\mathbf{M}_c|$ small compared with unity, the curve giving the distribution of intensity therefore shows a peak at $\nu = \nu_c$, whose sharpness increases as $M_n/|\mathbf{M}_c|$ diminishes.

Assuming $M_n/|\mathbf{M}_c|$ to be small, the incoherent radiation thus gives a Compton line which is only slightly broadened. We can easily find the intensity of this line. It follows from (16) and (16')* that only the first term \mathbf{E}_0 in the bracket $\{ \}$ of (15) is to be taken into account. According to § 1, there are $\nu h^{-3} d\tau$ eigenfunctions corresponding to the element $d\tau$ of the momentum space. The total intensity of the radiation scattered in the direction \mathbf{n}' is therefore

$$I = I_0 \frac{\epsilon^4}{\mu^2 c^4} \frac{\sin^2(\mathbf{E}_0, \mathbf{n}')}{R^2} \frac{\nu_c^2}{\nu^2} \frac{\mu c^2}{E_c} \cdot \frac{h^6}{v} \cdot \frac{v}{h^3} \int \left| C_{\mathbf{M}' + \kappa'\mathbf{n}' - \kappa\mathbf{n}}^{(n)} \right|^2 d\tau. (18)$$

I_0 is the intensity of the incident radiation, R the distance from the atom, E_c the value of E' corresponding to \mathbf{M}_c . We make the transformation $\mathbf{M}' = \mathbf{m} + \mathbf{M}_c$ of the coordinates in momentum space. According to (16) and (16') the determinant $\frac{d(\mathbf{m}_x, \mathbf{m}_y, \mathbf{m}_z)}{d(\mathbf{M}_x', \mathbf{M}_y', \mathbf{M}_z')}$ has the value $\mu c^2 \nu / E_c \nu_c$. Therefore (cf. (11'))

$$I = I_0 \frac{\epsilon^4}{\mu^2 c^4} \frac{\sin^2(\mathbf{E}_0, \mathbf{n}')}{R^2} \left(\frac{\nu_c}{\nu} \right)^3.$$

This is the intensity formula for the Compton effect of a free electron, given by Breit, Dirac, and Gordon†.

* Since $\mathbf{E}_0 \cdot \mathbf{n} = 0$ and $\mathbf{n}' \times \mathbf{n}' = 0$.

† G. Breit, Phys. Rev. xxvii. p. 362 (1926). P. A. M. Dirac, Proc. Roy. Soc. (A) iii. p. 705 (1926). Gordon, *loc. cit.*

We have found that the second term in the bracket [] of (7) does not give any contribution to the intensity of the pure Compton effect. Taking previous considerations into account it may be expected that this term can only give a small contribution to the scattered radiation if the condition $h\nu > -E_1'$ is fulfilled. Making the further assumption that the frequency displacement due to the Compton effect is small compared with ν , it is easily found that the total intensity of the radiation scattered in any direction is given by the formula of J. J. Thomson*.

This result is not valid if the atom contains more than one electron. It is a well-known fact that a good approximation to the motion of the electrons in an atom is often obtained by assuming the field acting upon each electron to be stationary. If this is the case the results given here may be applied to each electron separately. For frequencies ν high compared with the ionization energies of all electrons, divided by h , the coherent scattering may be deduced classically from that distribution of charge which is given by the sum of the Schrödinger densities for each separate electron.

Using general principles of quantum mechanics, a more complete examination of the scattering problem for an atom containing more than one electron may be given.

The general results given here in some respects ought to be completed. More definite results may be obtained for special atoms, *e. g.* for the hydrogen atom.

I wish to express my thanks to Prof. N. Bohr, Prof. C. G. Darwin, and Dr. O. Klein for their valuable interest in this work. I am also indebted to Prof. W. L. Bragg for discussions about this problem.

CIV. Cavitation in Screw Propellers.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the July 1927 issue of the Philosophical Magazine a paper is presented by Mr. John Tutin entitled "A Theoretical Investigation of the Phenomenon of Cavitation in Screw Propellers," in which a new theory of flow about propellers is set forth. On page 23 it is stated that "the logical conclusion of this investigation is that an actuator cannot be made to deliver thrust by

* Cf. G. Wentzel, *loc. cit.*, and I. Waller, *loc. cit.*

the assumption of a perfect 'Bernoulli' flow and a discontinuity of pressure. It follows that the familiar Rankine-Froude theory and the corresponding vortex theory are incorrect. The inflow velocity and ideal efficiency deduced therefrom are misleading. This result is important, because these theories are extensively used in air-screw research in this country, France, Italy, Germany, and U.S.A."

We wish to call attention to the fact that the new theory rests upon an assumption which is not required in the Rankine-Froude theory, and which seems to us to have no experimental foundation. The assumption, not explicitly stated by the author, is contained in the left-hand member of equation 6 on page 21, which gives the longitudinal force acting on the inflow column. This force must be found by integrating the longitudinal component of the pressure over the entire boundary of the inflow column. The author's result is true only if the pressure is equal to p_0 everywhere on the boundary except at the propeller disk. In the general case the pressure outside of the slip-stream varies in such a way that $p + 1/2\rho V^2$ is constant as shown by Stanton and Marshall (see Repts. and Memo. No. 460 of the British Aeronautical Research Committee), and the longitudinal force depends on the shape of the boundary and on the area of the inflow column at a great distance from the screw. There is then no inconsistency with Equation 2. We know of no experiments which indicate that the pressure on the boundary of the inflow column is constant and equal to p_0 .

In connexion with the phenomenon of cavitation of water propellers, it may be of interest to call attention to the fact that the occurrence of a somewhat similar phenomenon in air propellers may be inferred from the results of our experiments on propeller sections at high speeds (see Technical Reports Nos. 207 and 255 of the National Advisory Committee for Aeronautics). It appears that a change of flow with speed takes place, which is dependent in some way on the flow very close to the surface—that is, in the "boundary layer." The lower limit of the pressure at any point on the surface seems to be of the order of one-half an atmosphere.

Yours faithfully,

Bureau of Standards,
Washington, D.C.
July 28, 1927.

L. J. BRIGGS,
H. L. DRYDEN.

CV. *Cavitation in Screw Propellers.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE Phil. Mag. vol. iv. July 1927 contains a paper by Mr. J. Tutin dealing with the cavitation of screw propellers, in which the author puts forward a modified treatment of the actuator disk of Froude and Rankine and derives a different expression for the efficiency of the propeller. Mr. Tutin, however, is not correct in his statement that the modern vortex theory of air-screws depends on this assumption of an actuator disk.

The conception of the actuator disk is clearly a simplified assumption of the true characteristics of an air-screw, and Mr. Tutin has obtained a result in discordance with modern theory by applying the conception outside the limits of its validity. In estimating the increase of total pressure head in the air-screw slip-stream, it is legitimate to use Mr. Tutin's equations (2) and (3), which neglect the radial component of the velocity at the air-screw disk; but this course is no longer sound when it is desired to consider independently the regions before and behind the air-screw. For a stream tube passing through the air-screw disk the equations should be

$$p_0 + \frac{1}{2}\rho V^2 = p + \frac{1}{2}\rho(V+u)^2 + \frac{1}{2}\rho w^2,$$

$$p + p_1 + \frac{1}{2}\rho(V+u)^2 + \frac{1}{2}\rho w^2 = p_0 + \frac{1}{2}\rho(V+v)^2,$$

where w is the radial component of the velocity. If the analysis is now continued on the lines suggested by Mr. Tutin, it follows that

$$u^2 = w^2 = (v-u)^2,$$

which is consistent with the modern theory that $v=2u$. Mr. Tutin's mysterious energy, which is lost in the inflow column and regained in the outflow column, is simply the kinetic energy of the radial velocity.

It follows that Mr. Tutin's modified expression for the air-screw efficiency cannot be accepted; but his later remarks on the nature and cause of cavitation give a correct description of the phenomenon. Cavitation occurs when the suction on the back of a blade is too intense; and to avoid cavitation it is necessary to obtain the thrust by pressure on the face of a blade rather than by suction on its back. Some such adjustment is possible by suitable choice of

the blade angles and camber of the blade sections. The problem, however, is further complicated by the rotation of the slip-stream which reduces the pressure at the core of the slip-stream.

Yours faithfully,

Royal Aircraft Establishment,
South Farnborough,
August 17, 1927.

H. GLAUERT.

CVI. *Cavitation in Screw Propellers.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I AM pleased to note that Messrs. Briggs and Dryden admit that my theory is correct if the pressure is equal to p_0 everywhere at the "boundary" except at the screw disk. That this assumption is implicit is quite clear from the equations, and it was not therefore considered necessary to state it separately. It is in my opinion a legitimate approximation to make. It is quite independent of the shape and extent of the slip-stream. It is doubtful whether in practice the "boundary" of the slip-stream can be precisely determined—certainly not by experiments in a wind tunnel, as I am sure Dr. Stanton would be the first to admit.

Indirectly, however, wind-tunnel experiments confirm the new momentum theory, because the mean experimental inflow ratios obtained independently by both Stanton and Fage are invariably greater than .5 (*e.g.* Fage, R. & M. No. 940, pp. 4 & 5 and Table 4).

In reply to Mr. Glaupert, I am aware that the assumptions made in the Froude-Rankine theory differ ostensibly from the assumptions of the Vortex theory. In regard to inflow ratio, however, the two theories give the same result, and in this respect they must obviously sink or swim together.

It can be shown that for the Froude-Rankine actuator, the suction on the fore side of the disk must be equal to or less than the excess pressure on the after side. In an actual propeller, the suction on the back of the blades is usually more than double the pressure on the face of the blades. It is palpably absurd to suppose that the Froude-Rankine

actuator can in this respect represent even approximately the "true characteristics of an air-screw."

My amendments permit of an actuator having any required pressure distribution between the two sides, and for this reason alone it is likely to give results more consistent with experimental observations than are the deductions of existing theories.

There is certainly some difficulty in giving the correct physical interpretation to the additional terms introduced in the equations. As Mr. Glauert points out, the term in equation (11) labelled "energy dissipated at screw-disk" must be regarded as energy supplied at the screw-disk. This correction does not affect the applications of the theory, but the efficiency expressions should of course be amended accordingly. I do not agree with Mr. Glauert that these terms should be regarded as representing the radial component of the velocity. If this were so, at zero speed of advance the stream-lines at the screw-disk would be inclined at an angle of 45 degrees to the plane of the disk.

I invite exponents of the vortex theory to account for the following observed facts, which the amended momentum theory adequately interprets:—

1. Observed inflow ratios are normally greater than the value $\cdot 5$ indicated by the vortex theory.
2. Thrust and torque integrations by the vortex theory are normally in excess of the measured thrust and torque, which indicates overestimation of the angle of incidence by the vortex theory. This corresponds to too small an inflow.
3. The vortex theory indicates zero inflow at zero thrust. This cannot be reconciled with the experimental pitch ratios less than unity, as observed by Mumford and Schaffran (*loc. cit.*).
4. At high revolutions and positive nominal slip, Admiral D. W. Taylor, U.S.N., has obtained in the Washington Experiment Tank zero thrust from a cavitating propeller. This can be accounted for by the new momentum theory as being due to *excessive* inflow, when by the vortex theory the inflow would be zero.

Yours faithfully,

JOHN TUTIN.

Department of Naval Architecture,
The Technical College, Sunderland.

GENTLEMEN,—

IN a communication on "The Effect of Radon on the Solubility of Lead Uranate" (Phil. Mag. vol. iv. p. 404, Aug. 1927), Dr. Kenneth C. Bailey ascribes to me the suggestion that in uranium minerals "most of the lead produced would probably form lead uranate, which is practically insoluble," while in thorium minerals "the relatively soluble lead thorate would be formed and partially removed by leaching." I wish to correct the erroneous impression that I contrasted the behaviour of lead uranate with that of "lead thorate." In the paper to which Dr. Bailey refers, I wrote (Phil. Mag. vol. i. p. 1068, May 1926):—"In thorium minerals the lead could not form a thorate, as thorium and oxygen do not constitute an acidic environment, and corresponding with this no thorates are known to exist. In thorianite the lead should be largely present as an oxide; and in thorite partly as oxide, and partly perhaps as a silicate. In both minerals the most probable lead compounds are therefore of a comparatively soluble type."

Dr. Bailey's experimental demonstration that under appropriate conditions lead from lead uranate may pass into solution must be taken into account in considering the alteration of radioactive minerals by weathering or ground-waters, but it does not effect the validity of my deduction that "lead present as oxide or silicate would be more easily removed by percolating waters and kinetic exchange than the lead in uranium minerals." Moreover, altered uraninites commonly give higher lead-ratios than the fresh materials associated with them, and at the same time have clearly lost a notable proportion of the uranium originally present. This indicates that under natural conditions leaching, when it occurs, removes uranium in greater proportion than lead. A repetition of Dr. Bailey's experiments B and C, using actual minerals instead of lead uranate, should provide a direct test of the principle of my preferential leaching hypothesis, and would probably give results that could be applied to the problem of interpreting discordant series of lead-ratios.

Yours faithfully,

ARTHUR HOLMES.

Science Laboratories,
The University, Durham.
August 12, 1927.

CVIII. *Notices respecting New Books.*

Thermionic Phenomena. By EUGÈNE BLOCH. Translated by J. R. CLARKE. (Methuen & Co. Price 7s. 6d. net.)

THE translation of Prof. Bloch's 'Les Phénomènes Thermioniques' should be of service as an introduction to one of the most important branches of modern physics. Reference is made to the researches of many investigators, in particular Prof. O. W. Richardson.

The first chapter gives interesting historical details of the subjects, the remaining part being devoted to electronic and positive ion emission in vacua and in gases, and the application of thermionic phenomena to the measurement of high vacua and to the rectification of alternating currents.

There are two useful indexes—one for authors, the other for subjects.

Light. By F. BRAY, M.A. (Edward Arnold & Co. Price 6s.)

THE author has successfully accomplished the task of providing an up-to-date text-book which will serve the purpose of general education, preparation for the Higher Schools Examinations, and the study of more advanced works on this subject. The historical treatment of the subject is a specially valuable feature, and will, without doubt, arouse the interest of the student.

The second part of the volume is devoted to the exposition of wave theory, with an introductory chapter on simple harmonic motion, interference, diffraction and polarization of light, and spectrum analysis.

The questions appended to each chapter serve to emphasize the most important points and to summarize the general results.

Mr. Bray has struck out a new line of treatment and produced a book noteworthy both for its freshness and utility.

History of Radio-Telegraphy and Telephony. By G. O. BLAKE, M.I.E.E., A.Inst.P. Pp. xix+425, with numerous figures. (London: Radio Press. 1926. n.p.)

THIS volume is not so much an historical account of the development of radio-telegraphy and telephony as a history of inventions connected with these sciences. The division into chapters is therefore mainly conditioned by the subjects under discussion: thus, for instance, one chapter deals with coherers, another with detectors, another with spark and arc generators of high-frequency currents, and so forth. The author has done his work with great thoroughness, and the reference list at the end of the volume contains 1125 entries. Many almost forgotten devices are recalled in the hope that, though of little practical use in their present form, they may contain ideas which may usefully be

adopted to some new invention. The volume is illustrated with over 200 illustrations of apparatus and circuits, extracted from patent specifications or technical journals. As a work of reference the volume should prove of considerable value, and its use will be facilitated by the detailed index at the end of it.

Spectroscopy. By E. C. C. BALY, C.B.E., M.Sc., F.R.S. Third Edition. In 4 volumes. Vol. II. Pp. viii+398, with 95 figures. (London: Longmans, Green & Co. 1927. Price 18s. net.)

THE numerous developments in spectroscopy during recent years are indicated by the fact that four volumes are required for the third edition of Prof. Baly's well-known work on 'Spectroscopy.' The first volume of the new edition appeared in 1924; the newer developments of the subject, arising in large measure from the application of quantum ideas by Bohr, will be dealt with in the two volumes which remain to be published. In the third volume it is proposed to include chapters on spectral series, the Zeeman and Stark effects and emission band spectra, whilst the fourth volume will deal with absorption spectra, the shift of spectral lines by pressure and by line-of-sight motion.

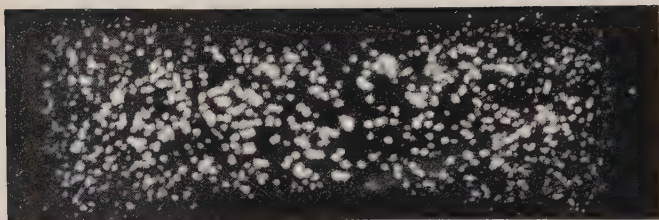
The volume under review contains an account of the application of interference methods to spectroscopy, including the theories of interferometers and special applications such as the determination of the angular diameters of stars, together with chapters on methods of illumination, the nature of spectra, fluorescence and phosphorescence, and the photography of the spectrum. Many investigations now demand a knowledge of the spectrum in the extreme infra-red and ultra-violet, and special plates and special methods of treatment are necessary. A great deal of valuable information is given on these matters, much of the information having been supplied by Dr. C. E. K. Mees.

The chapter on illumination includes an account of King's electric resistance furnace spectra and of the explosion of wires, and contains many practical details of great value for the experimental spectroscopist. The chapter on fluorescence and phosphorescence is very complete, and includes accounts of the most recent work on the subject.

Spectroscopists will look forward with eagerness to the appearance of the two remaining volumes, and we may venture a hope that publication will not be unduly delayed.

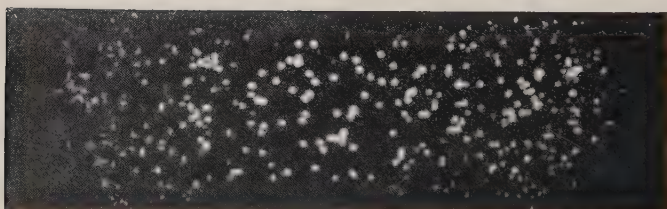
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

GREEN.



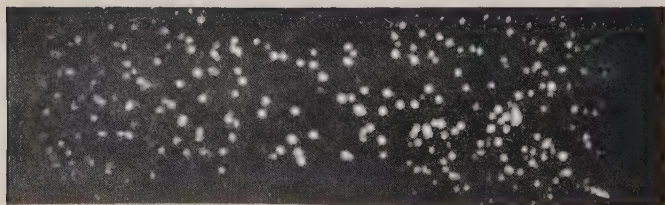
6 MINUTES.

5.53×10^5 particles per c.c.



30 MINUTES.

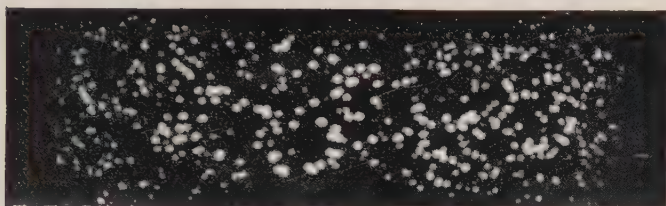
2.62×10^5 particles per c.c.



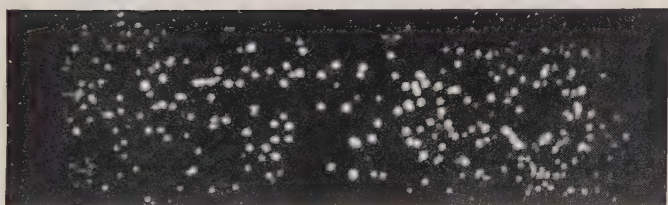
65 MINUTES.

1.60×10^5 particles per c.c.

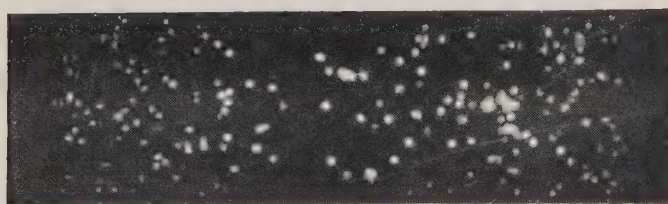
DROPLETS FORMED BY THE CONDENSATION OF MOISTURE ON



20 MINUTES.
 3.54×10^5 particles per c.c.

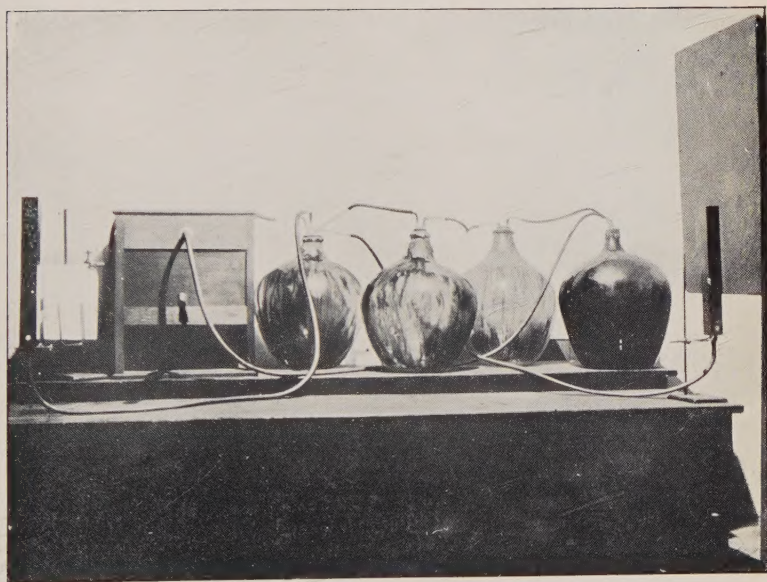


50 MINUTES.
 1.94×10^5 particles per c.c.



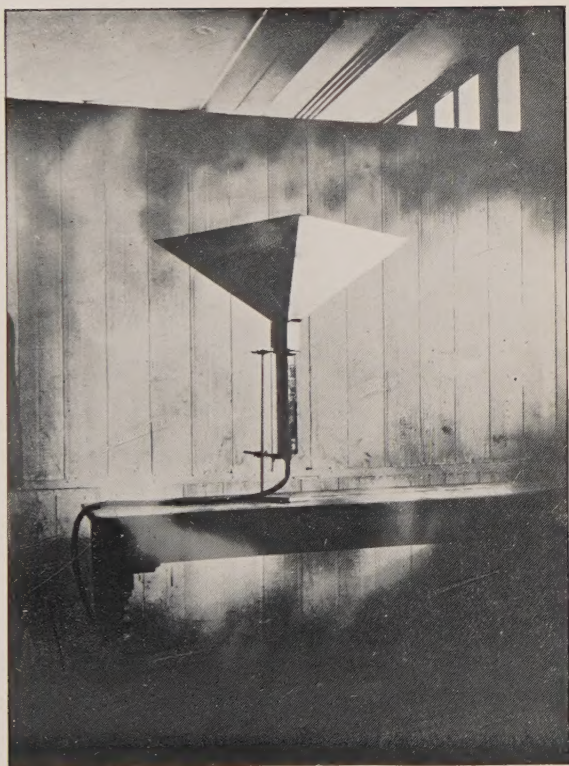
90 MINUTES.
 1.19×10^5 particles per c.c.

FIG. 1



General view of apparatus used in experiments.

FIG. 3.



View of "Hopper" flange on pipe.

